Theoretical study of structural properties and dissociation pathways of FCN and ClCN

I. Bhattacharyya, N.C. Bera, and A.K. Das[a]

Department of Spectroscopy, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India

Abstract. Geometrical parameters, harmonic frequencies and molecular properties of FCN, ClCN, their cations and the isomers of FCN and ClCN are studied in detail using ab initio MP2, CCSD and CCSD(T) methods. The dissociation energy of FCN and ClCN in various dissociation channels has been investigated. Both ground and metastable state of the fragmented atoms are considered in their dissociation pathways. The isomerization energy of FCN and ClCN and the NBO charges of FCN, ClCN, their cations and isomers are analyzed.

PACS. 31.15.Ar Ab initio calculations – 31.15.Ew Density-functional theory – 33.15.Dj Interatomic distances and angles – 33.15.Fm Bond strengths, dissociation energies – 33.15.Ry Ionization potentials, electron affinities, molecular core binding energy

1 Introduction

Chlorine and fluorine containing molecules have special interest in atmospheric science because these molecules are involved in the depletion of ozone layer in the stratosphere. The depletion of ozone layer is caused by the reaction of ozone with fluorine and chlorine that released from the fluorine and chlorine containing molecules through various dissociation pathways. In the stratosphere, there is a variation of temperature depending upon the region of the atmosphere above the surface of the earth. At 10 to 15 km from the surface of the earth the temperature begins to rise and above that region the temperature generally decreases. In this varying temperature region there is a possibility that the fragmented atoms after dissociation exist either in ground state or in their metastable state. More discussions on this topic in the context of astrophysics are now available [1–3]. In this article, we have studied the dissociation channels of FCN and ClCN along with the structural properties of FCN, ClCN, their cations and isomers. The ab initio MP2, CCSD and CCSD(T) methods are applied to study their properties. The correlation consistent valence triple-zeta basis set is used in this calculation. The theoretical and experimental works so far reported in the literature are on the structural properties of FCN, ClCN and their cations and isomers. Lee and Racine [4] performed a coupled-cluster study of the molecular structure, vibrational spectrum and relative energies of FCN, ClCN and their isomers using TZ2P basis set. Later, Lee et al. [5] and Wang

et al. [6] applied CCSD(T) method in conjunction with cc-pVTZ and 6-311G(2d) basis set respectively to study the structural properties of FCN and ClCN molecules. Bogey et al. [7] used mm and sub-mm spectroscopy to study FCN molecule and reported harmonic vibrational frequencies. Saouli et al. [8] reported the Fourier-Transform Infrared spectra of ClCN. Degli-Esposti et al. [9] observed both low and high frequency rotational spectra of FCN in the centimeter and millimeter wave region using Stark modulated and source modulated spectrometer and a Fabry-Perot type of interferometer. Lafferty and Lide [10] assigned the lines of the microwave spectra of FCN obtained on a conventional Stark modulated spectrometer at room temperature. Whiffen [11] supported the frequencies and rotational constants of FCN, estimated from his observed spectra, by direct diagonalization of the Hamiltonian matrix. Tyler and Sheridan [12] determined the structural parameters of FCN from the microwave spectra. Wang and Overend [13] have calculated the force constants in the general quartic valence force field of FCN and ClCN using the simplified model of Anderson. The parameters of the model were adjusted by least square fit to the experimental data from the microwave and infrared spectra and the parameters so obtained were then used to calculate the force constant and from these, vibrational energies and rotational constants. Murchison and Overrend [14] reported the infrared spectra of ClCN, which is free from interference, at high resolution with the 2.5 mm vacuum grating spectrometer. Celii et al. [15] and Rosselein and Maier [16] recorded the laser excitation fluorescence spectra of $ClCN^+$ and estimated its equilibrium bond lengths and harmonic frequencies. Grieman et al. [17] reported

[a] e-mail: spakd@iacs.res.in

Table 1. Geometrical parameters, zero-point energy, vibrational frequencies and dipole moment of FCN.

Optimized parameters	MP2	CCSD	CCSD(T)	Other values
R(F-C) (Å)	1.27	1.27	1.27	1.26[a], 1.275[b], 1.27[c]
R(C-N) (Å)	1.17	1.15	1.16	1.16[a,b,c]
ZPE (eV)	0.26	0.28	0.27	
ω_1 (cm^{-1})	456.30 (6.59)*	471.97 (8.16)	450.60	432[b], 442[c], 451[d], 450.92[e], 451[f]
ω_2 (cm^{-1})	1074.16 (58.60)	1104.23 (58.39)	1078.47	1060[b], 1056[c], 1079[d], 1076.52[e], 1076[f], 1069.4[g]
ω_3 (cm^{-1})	2277.52 (76.14)	2422.87 (92.26)	2350.36	2331[b], 2322[c], 2350[d], 2318.81[e], 2319[f], 2323[h]
Dipole moment (D)	2.31	2.17	2.29	
IP (eV)	13.56	13.07	13.13	
EA (eV)	0.42	0.22	0.20	

[a] Expt. value, reference [9]; [b] CCSD(T)/TZ2P value, reference [4]; [c] CCSD(T)/6-311G(2d) value, reference [6]; [d] CCSD(T)/cc-pVTZ value, reference [5]; [e] expt. values, references [11,13]; [f] expt. value, reference [7]; [g] expt. value, reference [10]; [h] expt. value, reference [12]; *IR intensity is given in the parenthesis.

the electron impact fluorescence spectra of ClCN$^+$ and determined its stretching frequencies only. Sommerfeld [18] studied the geometries and vibrational frequencies of FCN and its isomer and anion using ab initio MP2, SDCI, CCSD and CCSD(T) methods. However, in all these theoretical and experimental works only geometrical parameters have been calculated but no attempt has been made so far to study the dissociation pathways of FCN and ClCN in the varying temperature region.

2 Computational details

The structural properties of FCN, ClCN, their cations FCN$^+$, ClCN$^+$, their isomers FNC and ClNC and the dissociation channels of FCN and ClCN are studied in detail using ab initio MP2, CCSD and CCSD(T) methods [19–24]. In the dissociation channels the fragmented atoms are considered to be either in their ground state or in their metastable states. Isomerization energy at ab initio levels and the NBO (Natural Bond Orbital) atomic charges at MP2/cc-pVTZ level are studied. The electron correlation effects have been taken into account via Moller-Plesset perturbation (MP) theory and coupled cluster techniques. The conventional ab initio method applied in this work are second order Moller-Plesset perturbation theory (MP2) and the coupled cluster CCSD and CCSD(T) methods. The CCSD(T) method includes single and double excitations and an estimate of triple excitations by a perturbation treatment where as the CCSD method incorporates only single and double excitations. The Gaussian 98 suite of quantum chemistry program [25,26] has been used to perform MP2, CCSD and CCSD(T) calculations. The correlated consistent cc-pVTZ basis set [27,28] has been used for C, N, F and Cl.

3 Results and discussion

The geometrical parameters of FCN are listed in Table 1 along with other theoretical and experimental values for comparison. The equilibrium FC and CN bond lengths agree very well with the existing theoretical and

experimental values. The frequency for the FC stretching mode (ω_2) agrees very well with the experimental values of Bogey et al. [7] and Wang and Overend [13]. It is observed from the existing theoretical data that the value of ω_2 increases from 6-311G(2d) basis set to TZ2P and then at cc-pVTZ basis set the CCSD(T) method reproduces the experimental values. The frequency for the CN stretching mode (ω_3) that increases with the improvement of basis set, is little higher than the experimental values. The frequency for the bending mode (ω_1) also agrees very well with the experimental values. It is observed from the Table that the frequency for all the three modes ω_1, ω_2 and ω_3 decreases from CCSD to CCSD(T); inclusion of triple excitations reduces their frequencies. It may be noted that the values for ω_1 and ω_2 at MP2 level is almost same to that at CCSD(T) level. The electron correlation does not affect much on the values of ω_1 and ω_2 whereas it has much effect on ω_3. The ionization potential (IP) decreases from MP2 to CCSD and it remains almost unchanged from CCSD to CCSD(T) level. The value of electron affinity (EA) at CCSD and CCSD(T) level is almost same which implies that the triple excitations have little effect on the electron affinity of FCN. The value of EA at CCSD(T) level is half of its value at MP2 level.

The geometrical parameters, zero point energy and vibrational frequencies of FCN$^+$ are displayed in Table 2 along with the only available theoretical value of Wang et al. [6]. The equilibrium bond lengths for FC and CN agree very well with the values of Wang et al. The calculated frequency for the FC stretching mode (ω_2) is higher than that of Wang et al. The frequencies for the other two modes, CN stretching mode (ω_3) and the bending mode (ω_1) are also higher than the existing theoretical values. As discussed in the last paragraph, the frequencies for the stretching and bending modes increase with the improvement of basis set and at the cc-pVTZ basis set CCSD(T) method gives the accurate values. The smaller 6-311G(2d) basis set used by Wang et al. [6] is not adequate to get accurate values.

The results for FNC are summarized in Table 3 along with the other theoretical data of Lee et al. [4,5] and Sommerfeld [18]. The equilibrium bond lengths and the frequency for the bending mode (ω_1) agree very well with

Table 2. Geometrical parameters, zero point energy, vibrational frequencies and dipole moment of FCN^+.

Optimized parameters	MP2	CCSD	CCSD(T)	Other values
R(F-C) (Å)	1.20	1.20	1.21	1.206[a]
R(C-N) (Å)	1.21	1.22	1.23	1.229[a]
ZPE (eV)	0.32	0.26	0.26	
ω_1 (cm^{-1})	374.78, 601.04, (52.72)*, (26.19)	396.10, 452.78, (60.78), (15.32)	358.22, 439.53	354.9[a], 437.1[a]
ω_2 (cm^{-1})	1342.26 (63.31)	1170.21 (61.35)	1151.81	1133.9[a]
ω_3 (cm^{-1})	2795.49 (382.65)	2218.79 (137.69)	2187.14	2159.8[a]
Dipole moment (D)	0.18	0.18	5.15	

[a] CCSD(T)/6-311G(2d) value, reference [6]; *IR intensity is given in the parenthesis.

Table 3. Geometrical parameters, zero point energy, vibrational frequencies and dipole moment of FNC.

Optimized parameters	MP2	CCSD	CCSD(T)	Other values
R(F-N) (Å)	1.30	1.30	1.31	1.31[a]
R(N-C) (Å)	1.19	1.17	1.18	1.18[a]
ZPE (eV)	0.22	0.23	0.21	
ω_1 (cm^{-1})	244.06 (0.02)*	219.19 (0.27)	200.84	200[a], 168.4[b]
ω_2 (cm^{-1})	987.20 (68.49)	997.44 (68.60)	948.01	948[a], 967.7[b]
ω_3 (cm^{-1})	2127.65 (0.57)	2248.01 (14.96)	2157.39	2158[a], 2237[b]
Dipole moment (D)	1.40	1.75	1.42	

[a] CCSD(T)/cc-pVTZ value, reference [5]; [b] CCSD value, reference [18]; *IR intensity is given in the parenthesis.

Table 4. Dissociation energies (in eV) of FCN molecule at various dissociation channels when atoms are in their ground state.

	Dissociation scheme			
Method	$C(^3P)+F(^2P)+N(^4S)$	$CF(^2\Pi)+N(^4S)$	$NF(^3\Sigma^-)+C(^3P)$	$CN(^2\Sigma^+)+F(^2P)$
MP2	13.26 eV	7.54 eV	10.09 eV	6.29 eV
CCSD(T)	12.39 eV	6.94 eV	9.36 eV	5.17 eV

Table 5. Dissociation energies (in eV) of FCN molecule at various dissociation channel when fragmented atoms are in their metastable state.

	Dissociation scheme			
Method	$C(^1D)+F(^4S)+N(^2D)$	$CF(^2\Pi)+N(^2D)$	$NF(^3\Sigma^-)+C(^1D)$	$CN(^2\Sigma^+)+F(^4S)$
MP2	45.76 eV	10.85 eV	12.03 eV	33.54 eV
CCSD(T)	43.35 eV	9.68 eV	10.82 eV	31.93 eV

the values of Lee et al. The CCSD values of Sommerfeld for ω_1, ω_2 and ω_3 are much lower than our CCSD values. The value of ω_1 decreases from MP2 to CCSD(T) which implies that the effect of electron correlation reduces the frequency gradually. The MP2 value for the FN stretching frequency (ω_2) is almost same to that of CCSD but it decreases about 50 cm^{-1} from CCSD to CCSD(T). The triple excitations reduce the frequency considerably. The effect of triple excitations is more on the NC stretching mode (ω_3) which decreases about 90 cm^{-1} from CCSD to CCSD(T). The isomerization energy (ΔE_1) of FNC, for the reaction FCN → FNC + ΔE_1, calculated by MP2, CCSD and CCSD(T) methods is 3.25 eV, 3.03 eV and 2.99 eV respectively. The value of isomerization energy (ΔE_1) decreases about 0.25 eV from MP2 to CCSD(T) method. Inclusion of electron correlation at different level of calculation gradually decreases the isomerization energy.

The dissociation energies of FCN molecule in various dissociation channels are shown in Table 4. In the dissociation pathways the fragmented atoms are in their ground state. The minimum energy obtained by CCSD(T)/cc-pVTZ method, has been observed for the dissociation channel $CN(^2\Sigma^+) + F(^2P)$. The highest dissociation energy is estimated for the dissociation channel where all the fragmented atoms are in their ground state.

In Table 5, the various dissociation pathways of FCN molecule have been studied where the fragmented atoms are in their metastable state. Among these dissociation channels the lowest energy has been calculated, at CCSD(T)/cc-pVTZ level, for the dissociation scheme $CF(^2\Pi) + N(^2D)$ and the highest dissociation energy has been estimated for the dissociation channel where all the fragmented atoms are in their metastable state. This situation is similar to that observed for the dissociation channel where all fragmented atoms are in their ground state.

Molecule/Ion	F	C	N
FCN	−0.08 (−0.24)	0.54 (0.63)	−0.46 (−0.39)
FCN$^+$	0.17 (−0.04)	0.80 (0.95)	0.03 (0.09)
FNC	−0.05 (−0.10)	−0.35 (0.16)	0.39 (−0.06)

Table 6. Calculated atomic charges. By ChelpG and NBO (in parenthesis) methods using electron density calculated at MP2/cc-pVTZ level, in atomic unit.

Table 7. Geometrical parameters, zero-point energy, vibrational frequencies and dipole moment of ClCN.

Optimized parameters	MP2	CCSD	CCSD(T)	Other values
R(Cl-C) (Å)	1.63	1.64	1.64	1.64[b]
R(C-N) (Å)	1.17	1.16	1.17	1.17[b]
ZPE (eV)	0.23	0.24	0.24	
ω_1 (cm^{-1})	384.65 (2.54)*	395.83 (3.24)	381.82	372.5[a], 382[b], 378.18[c], 381.91[d]
ω_2 (cm^{-1})	754.55 (8.92)	749.54 (6.06)	737.80	713[a], 738[b], 740.82[c], 747.99[d]
ω_3 (cm^{-1})	2139.38 (13.18)	2318.78 (21.83)	2241.87	2227.9[a], 2242[b], 2228.21[c], 2248.96[d]
Dipole moment (D)	3.07	2.81	3.03	
IP (eV)	12.79	12.17	12.20	
EA (eV)	−0.33	−0.67	−0.64	

[a] CCSD(T)/6-311G(2d) value, reference [5]; [b] CCSD(T)/cc-pVTZ value, reference [6]; [c] FTIR value, reference [8]; [d] IR value, reference [14]; *IR intensity is given in the parenthesis.

Table 8. Geometrical parameters, zero-point energy, vibrational frequencies and dipole moment of ClCN$^+$.

Optimized parameters	MP2	CCSD	CCSD(T)	Other values
R(Cl-C) (Å)	1.56	1.57	1.57	1.58[a], 1.56[b]
R(C-N) (Å)	1.19	1.21	1.21	1.21[a], 1.22[b]
ZPE (eV)	0.29	0.22	0.22	
ω_1 (cm^{-1})	340.38, 519.93, (16.76)*, (5.94)	347.88, 393.46, (16.38), (2.87)	254.31, 334.65	315.3[a], 375.2[a]
ω_2 (cm^{-1})	912.29 (14.82)	837.73 (28.63)	833.96	800.2[a], 827[b], 823[c]
ω_3 (cm^{-1})	2897.20 (7.06)	2040.04 (12.58)	2062.42	1959.8[a], 1915[b,c]
Dipole moment (D)	0.99	1.25	3.74	

[a] CCSD(T)/6-311G(2d) value, reference [6]; [b] expt. value, reference [16]; [c] expt. value, reference [17]; *IR intensity is given in the parenthesis.

The calculated atomic charges on F, C and N are shown in Table 6 for FCN, FCN$^+$ and FNC. For FCN molecule, the NBO charges on F and N are negative because F and N atoms are more electronegative than C and hence they attract electrons from C atom. Similar situation is noticed for FNC molecule. For FCN$^+$ molecule, N atom is positively charged and F atom is negatively charged due to its high electronegativity.

The structural parameters of ClCN are compared with other theoretical and experimental values in Table 7. The ClC and CN equilibrium bond lengths agree very well with the theoretical results of Lee et al. [4,5]. The CCSD(T) frequency for the bending mode (ω_1) agrees very well with IR experimental value of Murchison and Overend [14] and also with the FTIR value of Saouli et al. [8]. It should be mentioned here that both method and basis set should be appropriate to take into account the effect of electron correlations and to get accurate values. The CCl stretching frequency (ω_2) also agrees very well with IR and FTIR values. The calculated frequency for the CN stretching mode (ω_3) is 14 cm^{-1} higher than the FTIR value which is 20 cm^{-1} lower than the IR value. From overall comparison with the experimental values for ω_1, ω_2 and ω_3, our CCSD(T) results support the IR values of Murchison and Overend [14]. The CCSD(T)/6-311G(2d) values for

ω_1, ω_2 and ω_3 of Wang et al. [6] are consistently lower than the corresponding experimental value and also than our value. The electron affinity (EA) of ClCN calculated by the three methods is negative and its value becomes double from MP2 to CCSD or CCSD(T). The effect of electron correlation is very important in the calculation of electron affinity because of involvement of molecule anion, which is a highly correlated system due to the attachment of an extra electron.

The results for ClCN$^+$ are displayed in Table 8 along with the other theoretical value of Wang et al. [6]. The equilibrium ClC and CN bond lengths are very close to the CCSD(T)/6-311G(2d) value of Wang et al. The Π bending mode, which is supposed to be degenerate, has been found to have non-degenerate frequencies at all levels of calculation. The difference between these two frequencies is maximum at MP2 level and minimum at CCSD level. The frequency for the CCl stretching mode (ω_2) agrees very well with the laser excitation fluorescence works of Rosselein et al. [16] and Grieman et al. [17]. The CCSD(T)/6-311G(2d) value of Wang et al. is lower than our results and also lower than the experimental values. The CCSD(T) frequency for the CN stretching mode (ω_3) is higher than the experimental values.

Table 9. Geometrical parameters, zero-point energy, vibrational frequencies and dipole moment of ClNC.

Optimized parameters	MP2	CCSD	CCSD(T)	Other values
R(Cl-N) (Å)	1.62	1.63	1.64	1.65[a], 1.64[b]
R(N-C) (Å)	1.19	1.18	1.18	1.18[a,b]
ZPE (eV)	0.21	0.21	0.20	
ω_1 (cm^{-1})	258.23 (0.004)*	244.92 (0.085)	235.02	188[a], 236[b]
ω_2 (cm^{-1})	734.87 (0.71)	733.94 (0.25)	706.99	688[a], 707[b]
ω_3 (cm^{-1})	2074.88 (41.91)	2185.78 (99.92)	2105.81	2098[a], 2105[b]
Dipole moment (D)	2.28	2.64	2.37	

[a] CCSD(T)/TZ2P value, reference [4]; [b] CCSD(T)/cc-pVTZ value, reference [5]; *IR intensity is given in the parenthesis.

Table 10. Dissociation energies (in eV) of ClCN molecule at various dissociation channels when atoms are in their ground state.

	Dissociation scheme			
Method	Cl(^{2}P)+C(^{3}P)+N(^{4}S)	ClC($^2\Pi$)+N(^{4}S)	ClN($^3\Sigma^-$)+C(^{3}P)	CN($^2\Sigma^+$)+Cl(^{2}P)
MP2	12.30 eV	8.31 eV	9.93 eV	5.34 eV
CCSD(T)	11.49 eV	7.61 eV	9.10 eV	4.27 eV

Table 11. Dissociation energies (in eV) of ClCN molecule at various dissociation channels when fragmented atoms are in their metastable state.

	Dissociation scheme			
Method	Cl(^{4}S)+C(^{1}D)+N(^{2}D)	ClC($^2\Pi$) +N(^{2}D)	ClN($^3\Sigma^-$)+C(^{1}D)	CN($^2\Sigma^+$)+Cl(^{4}S)
MP2	33.86 eV	11.62 eV	11.88 eV	21.64 eV
CCSD(T)	31.85 eV	10.36 eV	10.56 eV	20.43 eV

The geometrical parameters of ClNC are given in Table 9. The theoretical results of Lee et al. [4,5] obtained by two different basis sets are given in the table for comparison. It is observed from the two reported values of Lee et al. that improvement of basis set from TZ2P to cc-pVTZ increases the values of frequency of the two stretching mode and the bending mode. The frequency for the bending mode (ω_1) and the ClN stretching mode (ω_2) decreases from MP2 to CCSD(T) whereas the NC stretching mode (ω_3) increases from MP2 to CCSD(T). The effect of triple excitations is maximum on ω_3 and minimum on ω_1. The results obtained by all three methods are very consistent. The isomerization energy (ΔE_2) of ClCN, for the reaction ClCN → ClNC + ΔE_2, obtained by MP2, CCSD and CCSD(T) is 2.09 eV, 1.86 eV and 1.86 eV respectively. The value of isomerization energy calculated at CCSD and CCSD(T) level is same which implies that triple excitations have no effect on the isomerization energy.

The dissociation pathways of ClCN are shown in Table 10. In these dissociation channels the fragmented atoms are in their ground state. Among four dissociation path ways the minimum energy pathway has been obtained for CN($^2\Sigma^+$) + Cl(^{2}P) and this energy is lower than that estimated for FCN at CCSD(T) level. If the energy of the dissociation channels of ClCN has been compared with the corresponding channel of FCN, it is observed that the dissociation energy of a channel of ClCN is lower than its corresponding one of FCN except for ClC($^2\Pi$) + N(^{4}S) channel, its energy is higher than CF($^2\Pi$)+ N(^{4}S) channel of FCN.

Table 12. Calculated atomic charges. By ChelpG and NBO (in parentheses) methods using electron density calculated at MP2/cc-pVTZ level, in atomic unit.

Molecule/Ion	Cl	C	N
ClCN	0.06 (0.14)	0.32 (0.15)	−0.38 (−0.29)
ClCN$^+$	0.59 (0.62)	0.36 (0.27)	0.05 (0.11)
ClNC	0.07 (0.29)	−0.32 (0.24)	0.25 (−0.53)

The dissociation energy of ClCN molecule at various dissociation channels are summarized in Table 11. In these channels, the fragmented atoms are in their metastable state after dissociation of ClCN. Among the four dissociation channels, the lowest energy pathway is ClC($^2\Pi$)+ N(^{2}D). Interestingly, another channel ClN($^3\Sigma^-$) +C(^{1}D) has been obtained whose dissociation energy is close to the lowest one. The dissociation energy of the earlier one is 0.2 eV lower than that of the latter. It may be noted here that for FCN molecule such situation has not been observed. The separation of energy between two dissociation channels of FCN is at least 1 eV. The highest dissociation energy is obtained for the channel where the ClCN molecule dissociates into the fragmented atoms in their metastable state.

The atomic charges on Cl, C and N atoms are displayed in Table 12 for ClCN, ClCN$^+$ and ClNC molecules. As shown in the Table for ClCN molecule, the NBO atomic charge on Cl is positive and that on N atom is negative. Although the electronegativity of N is little lower than that of Cl, N attracts more electrons from C atom that Cl. Similar situation is observed for the isomer ClNC

molecule, the NBO atomic charge on N is negative whereas the atomic charge on Cl is positive.

4 Conclusion

The structural properties such as equilibrium bond lengths, zero point energy, vibrational frequencies, dipole moment, ionization potential (IP) and electron affinity (EA) of FCN, ClCN, their cations FCN^+ and $ClCN^+$ and their isomers FNC and ClNC have been studied in detail using the ab initio MP2, CCSD and CCSD(T) methods. The dissociation energies of FCN and ClCN in various dissociation pathways have also been studied using these ab initio methods. The structural properties of all the molecules, particularly those for FCN^+, $ClCN^+$ and the isomerization energy of FCN and ClCN have been predicted very accurately for first time. The effect of electron correlation on the structural properties of FCN, ClCN, their cations and isomers have been discussed in great detail and the drawbacks of earlier calculations have been rectified. The NBO analysis of atomic charges on F, Cl, C and N has been made to show the change of atomic charge from neutrals to isomers. The dissociation pathways of FCN and ClCN, when the fragmented atoms are in the metastable state, have been studied for the first time. In the dissociation processes of FCN and ClCN the fragmented atoms have been considered to be either in the ground state or in the metastable state. Among various dissociation channels of ClCN when fragmented atoms are in their metastable state, the dissociation energy of ClCN at two dissociation pathways has been found to be very close.

References

1. S. Soloman, Rev. Geophys. **37**, 275 (1999); S. Soloman, Rev. Geophys. **26**, 131 (1988)
2. D. McNally, in *Advances in Atomic and Molecular Physics*, edited by D.R. Bates, I. Esterman (Academic Press, New York 1970), Vol. 8, p. 2
3. J.N. Bardsley, M.A. Biondi, in *Advances in Atomic and Molecular Physics*, edited by D.R. Bates, I. Esterman (New York, Academic Press, 1972), Vol. 6, p. 1
4. T.J. Lee, S.C. Racine, Mol. Phys. **84**, 717 (1995)
5. T.J. Lee, J.M.L. Martin, C.E. Dateo, P.R. Taylor, J. Phys. Chem. **99**, 15858 (1995)
6. D.C. Wang, F.T. Chau, E.P.F. Lee, A.K.M. Leung, J.M. Dyke, Mol. Phys. **93**, 995 (1998)
7. M. Bogey, A. Farkhsi, F. Remy, I. Dubois, H. Bredohl, A. Fayt, J. Mol. Spectros. **170**, 417 (1995)
8. A. Saouli, I. Dubois, J.F. Blavier, H. Bredohl, G. Blanquet, C. Meyer, F. Meyer, J. Mol. Spectros. **165**, 349 (1994)
9. C. Degli Esposti, P.G. Favero, S. Serenellini, G. Cazzoli, J. Molec. Struct. **82**, 221 (1982)
10. W.J. Lafferty, D.R. Lide Jr, J. Mol. Spectros. **23**, 94 (1967)
11. D.H. Whiffen, Spectrochim. Acta A **34**, 1173 (1978)
12. J.K. Tyler, J. Sheridan, Trans. Faraday Soc. **59**, 2661 (1963)
13. V.K. Wang, J. Overend, Spectrochim. Acta A **29**, 1623 (1973)
14. C.B. Murchison, J. Overend, Spectrochim. Acta A **27**, 2407 (1971)
15. F.G. Celli, J. Fulara, J.P. Maier, R. Rosslein, Chem. Phys. Lett. **131**, 325 (1986)
16. M. Rosselein, J.P. Maier, J. Phys. Chem. **93**, 7342 (1989)
17. F.J. Grieman, A. McIIroy, J. Perkins, J.J. Chem. Phys. **84**, 2481 (1986)
18. T. Sommerfeld, Phys. Chem. Chem. Phys. **3**, 2394 (2001)
19. R.J. Bartlett, Ann. Rev. Phys. Chem. **32**, 359 (1981)
20. A. Szabo, N.S. Ostlund, *Modern Quantum Chemistry* (McGraw-Hill, New York, 1998); and references therein
21. J. Cizek, Adv. Chem. Phys. **14**, 35 (1969)
22. G.D. Purvis III, R.J. Bartlett, Chem. Phys. **76**, 1910 (1982)
23. G.E. Scuseria, C.L. Janssen, H.F. Schaefer III, J. Chem. Phys. **89**, 7382 (1988)
24. J.A. Pople, M. Head-Gordon, K. Raghavachari, J. Chem. Phys. **87**, 5968 (1987)
25. M.J. Frisch et al., *Gaussian98* (Gaussian, Inc., Pittsburgh, PA, 1998)
26. J.B. Forseman, M.J. Frisch, *Exploring Chemistry with Electronic Structure Methods* (Gaussian, Inc., Pittsburgh, PA, 1996)
27. T.H. Dunning Jr, J. Chem. Phys. **90**, 1007 (1989)
28. D.E. Woon, T.H. Dunning Jr, J. Chem. Phys. **98**, 1358 (1993)