

# Accurate *ab Initio* Quartic Force Fields, Vibrational Frequencies, and Heats of Formation for FCN, FNC, ClCN, and ClNC

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The XCN and XNC ( $X = \text{F}, \text{Cl}$ ) isomers have been investigated using the CCSD(T) method in conjunction with correlation consistent basis sets. Equilibrium geometries, harmonic frequencies, anharmonic constants, fundamental frequencies, and heats of formation have been evaluated. Agreement with experiment for the fundamental frequencies is very good, even for  $\nu_2$  for ClCN, which is subject to a strong Fermi resonance with  $2\nu_3$ . It is also shown that a second-order perturbation theory approach to solving the nuclear Schrödinger equation gives results in excellent agreement with essentially exact variational calculations. This is true even for  $\nu_2$  of ClCN, provided that near-singular terms are eliminated from the perturbation theory formulas and the appropriate Fermi interaction energy matrix is then diagonalized. A band at  $615 \text{ cm}^{-1}$ , tentatively assigned as the Cl–N stretch in ClNC in matrix isolation experiments, is shown not to be due to ClNC. Accurate atomization energies are determined and are used to evaluate accurate heats of formation ( $3.1 \pm 1.5$ ,  $33.2 \pm 1.5$ ,  $72.6 \pm 1.5$ , and  $75.9 \pm 1.5 \text{ kcal/mol}$  for FCN, ClCN, FNC, and ClNC, respectively). It is expected that the theoretical heats of formation for FCN, FNC, and ClNC are the most accurate available.

## Introduction

The equilibrium structures, harmonic frequencies, and isomeric energy differences of the XCN and XNC ( $X = \text{F}, \text{Cl}$ ) molecules were the subject of a recent investigation,<sup>1</sup> hereafter referred to as paper I. Obtaining more complete gas-phase data on several fluorine and chlorine compounds that are of potential importance in stratospheric ozone depletion chemistry has been the subject of numerous recent studies from this laboratory (e.g., see refs 1–4 and references therein), and that was indeed the motivation for paper I. Although a very sophisticated electron correlation method was used [the singles and doubles coupled-cluster method with a perturbational treatment of connected triple excitations, denoted CCSD(T)] together with a triple- $\zeta$  double-polarized (TZ2P) basis set in paper I, there remained at least one issue that could not be definitively resolved. That is, a band at  $615 \text{ cm}^{-1}$  observed in matrix isolation experiments<sup>5</sup> was tentatively assigned as  $\nu_2(\sigma)$  of ClNC, but there was considerable uncertainty about this assignment. In paper I the CCSD(T)/TZ2P harmonic frequency was obtained as  $688 \text{ cm}^{-1}$ , and considering the accuracy of the TZ2P basis set, potential shifts due to the matrix environment, and the neglect of anharmonicity, the assignment of the  $615 \text{ cm}^{-1}$  band could not be ruled out, although it seemed unlikely to be correct. Thus one purpose of the present study is to determine a set of very accurate fundamental vibrational frequencies for ClNC and then

to resolve definitively whether or not the  $615 \text{ cm}^{-1}$  band is the Cl–N stretch of ClNC.

A second purpose of the present study is to compare the second-order perturbation theory and exact variational methods for solving the nuclear Schrödinger equation for fundamental vibrational frequencies. The ClCN molecule is of special interest here due to the known larger Fermi type I resonance between  $\nu_2$  (Cl–C stretch) and  $2\nu_3$  (ClCN bend). For the second-order perturbation theory method, the usual approach is used to account for the large Fermi resonance. That is, the near-singular terms are removed from the formulas for the anharmonic constants and the appropriate energy matrix is then diagonalized. The interested reader is referred to ref 6 and references therein for a recent discussion of how to treat Fermi resonances properly and an improved testing method to determine whether or not a Fermi resonance is significant enough that it requires a proper treatment. In this regard, it is also of interest to compare with a very recent experimental study<sup>7</sup> in which the ClCN Fermi resonance was treated in detail.

It should be noted that Botschwina *et al.*<sup>8</sup> have recently presented CEPA force fields for the FCN and FNC molecules that are moderately accurate. The CCSD(T) force fields presented in the present study are shown to yield vibrational transition frequencies in much better agreement with experiment and are therefore concluded to be more accurate. Given the established accuracy of the CCSD(T) method (e.g., see ref 9 and references therein), this conclusion is not unexpected.

A third purpose of the present study is to determine accurate

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**TABLE 1: CCSD(T) Energies (hartrees), Equilibrium Structures, Rotational Constants (MHz), Harmonic Frequencies (cm<sup>-1</sup>), Fundamental Frequencies (cm<sup>-1</sup>), and Anharmonic Constants (cm<sup>-1</sup>) of XCN<sup>a</sup>**

	FCN				C1CN			
	cc-pVDZ	cc-pVTZ	cc-pVQZ	expt <sup>b</sup>	cc-pVDZ	cc-pVTZ	cc-pVQZ	expt <sup>c</sup>
<i>E</i>	0.197802	0.381097	0.438365		0.237763	0.398013	0.447504	
<i>r</i> <sub>XC</sub>	1.2826	1.2701	1.2670	1.264	1.6604	1.6437	1.6384	1.629
<i>r</i> <sub>CN</sub>	1.1779	1.1632	1.1596	1.157	1.1800	1.1656	1.1619	1.160
<i>A<sub>e</sub></i>		10479		10554		5895		5971
$\omega_1(\sigma)$ C–N str		2350				2242		
$\omega_2(\sigma)$ X–C str		1079				738		741
$\omega_3(\pi)$ XCN bend		451				382		378
$\nu_1(\sigma)$ C–N str		2312		2319		2209		2216
$\nu_2(\sigma)$ X–C str		1077		1076		707 <sup>d</sup>		714
$\nu_3(\pi)$ XCN bend		446		451		379		379
<i>X</i> <sub>11</sub>		–12.729				–12.296		
<i>X</i> <sub>12</sub>		–1.306				–2.161		
<i>X</i> <sub>13</sub>		–12.511				–7.325		
<i>X</i> <sub>22</sub>		–6.422				–3.045		–3.190
<i>X</i> <sub>23</sub>		11.680				–2.923		–2.712
<i>X</i> <sub>33</sub>		–2.354				0.713		0.618
<i>G</i> <sub>33</sub>		3.081				–0.265		–0.166

<sup>a</sup> The energy is reported as  $-(E + 192)$  for FCN and as  $-(E + 552)$  for C1CN. Bond lengths in Å. The *r<sub>c</sub>* bond lengths for FCN are 1.2731 and 1.1643 Å, and for C1CN they are 1.6474 and 1.1652 Å. <sup>b</sup> Fundamental frequencies from ref 25; vibrationally averaged rotational constant from ref 23; equilibrium geometry from ref 21. <sup>c</sup> Vibrationally averaged rotational constant and  $\nu_1$  from ref 24; equilibrium geometry from ref 22; all other data from ref 7. <sup>d</sup> Subject to a strong Fermi resonance with  $2\nu_3$ —see text.

heats of formation of the FCN, FNC, C1CN, and C1NC molecules. In paper I accurate isomerization energies were determined, but these were not placed on an absolute scale. The available experimental heats of formation of the XCN molecules have large uncertainties, and experimental values for the XNC species do not exist. In particular, the heat of formation of FCN is uncertain by 4 kcal/mol.<sup>10</sup> In order to assess better the thermal stability and the importance of these molecules to atmospheric chemistry, it would be helpful to reduce these uncertainties. It is now often possible to obtain accurate atomization energies of many molecules using a combination of *ab initio* calculations and empirical data. Two approaches have been adopted in the present study. The first was recently proposed by Martin,<sup>11</sup> and the second involves an extrapolation technique proposed by Woon.<sup>12</sup> These will be described in more detail later.

### Computational Methods

Dunning's correlation consistent basis sets<sup>13</sup> have been used in the present study. Specifically, equilibrium geometries have been obtained with the cc-pVDZ and cc-pVTZ basis sets, and the harmonic frequencies and cubic and quartic force fields have been determined with the cc-pVTZ basis set. The cc-pVTZ basis set includes up to f basis functions on all heavy atoms. Equilibrium geometries of FCN and C1CN have also been obtained with the cc-pVQZ basis set. Only the pure spherical harmonic components of the basis functions have been included. The electronic structure method that has been used in all calculations is the closed-shell singles and doubles coupled-cluster method that includes a perturbational estimate of the effects of connected triple excitations, denoted CCSD(T).<sup>14</sup> This method has proven to yield very reliable bond distances, vibrational frequencies, bond energies, and other molecular properties when used in conjunction with large one-particle basis sets; for example, see ref 9 and references therein. The C, N, and F 1s-like molecular orbitals and the Cl 1s2s2p-like molecular orbitals have been required to remain doubly occupied in the correlation procedure (i.e., the frozen core approximation). The CCSD(T) energies were obtained with the TITAN<sup>15</sup> coupled-cluster program interfaced to the MOLCAS2<sup>16</sup> integrals (known as SEWARD<sup>17</sup>), self-consistent field, and transformation programs. These calculations were run on an RS/6000 model 365 workstation running at Limburgs Universitair Centrum.

**TABLE 2: CCSD(T) Energies (hartrees), Equilibrium Structures, Rotational Constants (MHz), Harmonic Frequencies (cm<sup>-1</sup>), Fundamental Frequencies (cm<sup>-1</sup>), and Anharmonic Constants (cm<sup>-1</sup>) of XNC<sup>a</sup>**

	FNC			C1NC		
	cc-pVDZ	cc-pVTZ	expt <sup>b</sup>	cc-pVDZ	cc-pVTZ	expt <sup>b</sup>
<i>E</i>	0.088115	0.269122		0.166127	0.328534	
<i>r</i> <sub>XN</sub>	1.3199	1.3097		1.6612	1.6371	
<i>r</i> <sub>NC</sub>	1.2011	1.1842		1.2009	1.1845	
<i>A<sub>e</sub></i>		10779			6303	
$\omega_1(\sigma)$ C–N str		2158			2105	
$\omega_2(\sigma)$ X–N str		948			707	
$\omega_3(\pi)$ XNC bend		200			236	
$\nu_1(\sigma)$ C–N str		2109	2123		2069	2074
$\nu_2(\sigma)$ X–N str		935	928		702	615?
$\nu_3(\pi)$ XNC bend		213			235	
<i>X</i> <sub>11</sub>		–14.255			–12.856	
<i>X</i> <sub>12</sub>		–3.005			–2.703	
<i>X</i> <sub>13</sub>		–18.369			–8.611	
<i>X</i> <sub>22</sub>		–8.386			–3.934	
<i>X</i> <sub>23</sub>		4.824			3.455	
<i>X</i> <sub>33</sub>		7.032			0.086	
<i>G</i> <sub>33</sub>		–1.611			0.925	

<sup>a</sup> The energy is reported as  $-(E + 192)$  for FNC and as  $-(E + 552)$  for C1NC. Bond lengths in Å. The *r<sub>c</sub>* bond lengths for FNC are 1.3125 and 1.1821 Å, and for C1NC they are 1.6413 and 1.1817 Å. <sup>b</sup> Reference 5.

Vibrational energy levels have been evaluated using two approaches. The second-order perturbation theory analyses have been determined using a modified version of the SPECTRO<sup>18</sup> package, while exact variational calculations have been performed using a program recently developed by Schwenke.<sup>19</sup>

### Results and Discussion

**A. Equilibrium Structures and Vibrational Frequencies.** The CCSD(T) equilibrium structures, harmonic frequencies, fundamental vibrational frequencies, and anharmonic constants for the FCN and C1CN molecules are presented in Table 1 while the analogous results for FNC and C1NC are given in Table 2. Where available, experimental values are presented for comparison. The  $\mathcal{T}_1$  diagnostic<sup>20</sup> values (0.015, 0.014, 0.020, and 0.021 for FCN, C1CN, FNC, and C1NC, respectively) indicate that the CCSD(T) method should perform well for these

molecules. Considering the XCN species first, it is shown that improvement of the one-particle basis set from cc-pVDZ to cc-pVTZ has a significant effect on the equilibrium bond distances, decreasing all of them by between 0.012 and 0.016 Å. These improvements are consistent with the results of a recent study in which CCSD(T)/cc-pVDZ and CCSD(T)/cc-pVTZ equilibrium geometries of several species were compared to accurate experimental values.<sup>11</sup> Comparison of the FCN CCSD(T)/cc-pVTZ equilibrium bond distances with the experimental<sup>21</sup> values exhibits the expected accuracy, while the CCSD(T)/cc-pVTZ equilibrium structure for ClCN suggests that the experimentally derived<sup>22</sup> geometry is somewhat in error. In particular, the experimental value for the Cl–C bond distance seems slightly too short while the experimental C–N bond distance is slightly too long. This assertion is further supported by comparison of the cc-pVQZ and experimental geometries—the agreement for FCN is quite reasonable, and consistent with earlier studies,<sup>9,11</sup> while the discrepancy for the Cl–C bond distance is much larger than expected. For both FCN and ClCN, the CCSD(T)/cc-pVTZ equilibrium rotational constant is in reasonable agreement with the experimental<sup>23,24</sup> vibrationally averaged value.

Comparison of the CCSD(T)/cc-pVTZ fundamental vibrational frequencies with the experimental<sup>7,24,25</sup> quantities shows that there is very good agreement for both FCN and ClCN—even for  $\nu_2(\sigma)$  of ClCN, which is subject to a large Fermi resonance with  $2\nu_3(\pi)$ . Indeed, the largest discrepancy between experiment and theory is only 7 cm<sup>-1</sup>. The agreement between experiment and theory in the present study is considerably better than that obtained by Botschwina *et al.*<sup>8</sup> with their CEPA force field, especially for the stretching motions (e.g., their largest error for a fundamental is 19 cm<sup>-1</sup>). Comparison of the CCSD(T) and CEPA force field parameters [CCSD(T) values given later] shows that the major differences seem to arise in the quadratic force constants and the off-diagonal cubic and quartic force constants. Interestingly, this is also true when comparing the CCSD(T) force field with an empirically derived one,<sup>26</sup> although the differences between the CCSD(T) and CEPA force fields are generally smaller than the differences between the CCSD(T) and empirical force fields. It would seem that the empirically derived force field is phenomenological in nature rather than being a true description of the physical system.

Due to the excellent agreement between the CCSD(T) and experimental fundamental frequencies, it is expected that the *ab initio* anharmonic constants contained in Table 1 are very accurate; there are no experimentally derived values for FCN with which to compare. For ClCN, Meyer *et al.*<sup>7</sup> have recently derived certain anharmonic constants and harmonic frequencies in their detailed study of the Fermi resonance between  $\nu_2$  and  $2\nu_3$ . The agreement between their empirical values and the CCSD(T) constants is very good in all cases (see Table 1). Another parameter that may be compared is the off-diagonal matrix element in the  $2 \times 2$  Fermi resonance matrix. This matrix element ( $k_{233}/\sqrt{2}$ ) is directly related to the cubic force constant in mass-weighted normal coordinates,  $k_{233}$ , in Nielsen notation. The CCSD(T)/cc-pVTZ value for  $k_{233}$ ,  $-46.064$  cm<sup>-1</sup>, leads to an off-diagonal matrix element of  $-32.572$  cm<sup>-1</sup>. Examination of Tables 6 and 7 from ref 7 leads to an empirical value of  $-32.806$  cm<sup>-1</sup>, again showing excellent agreement with the theoretical value. Given this excellent agreement, it is expected that the remaining CCSD(T)/cc-pVTZ anharmonic constants have similar accuracy, and it is hoped that these will be useful in the analysis of future experimental spectra. The agreement between experiment and the CCSD(T)/cc-pVTZ *ab initio* data for the XCN species also bolsters confidence in the

TABLE 3: Symmetry Unique Force Constants in BLBA Coordinates<sup>a</sup>

	FCN	FNC	ClCN	CINC
$f_{11}$	8.973 422	6.830 591	5.216 488	4.769 760
$f_{21}$	0.055 139	-0.575 260	0.110 292	-0.150 580
$f_{22}$	17.638 096	15.142 236	17.549 983	15.552 502
$f_{33}$	0.383 957	0.086 026	0.354 712	0.148 224
$f_{111}$	-59.997 054	-50.371 292	-28.344 549	-28.149 791
$f_{211}$	-1.953 973	-0.882 325	-1.451 849	-1.502 939
$f_{221}$	-0.443 791	1.538 145	-0.209 624	0.505 591
$f_{222}$	-119.960 638	-103.945 705	-118.076 892	-104.765 777
$f_{331}$	-0.639 664	-0.526 677	-0.551 240	-0.554 527
$f_{332}$	-1.303 588	-1.205 178	-0.854 486	-0.861 590
$f_{1111}$	341.315 962	278.543 022	130.189 449	129.268 600
$f_{2111}$	7.250 701	9.017 262	3.846 117	7.194 844
$f_{2211}$	1.885 163	3.718 416	0.600 821	1.429 151
$f_{2221}$	0.819 641	1.808 436	-1.204 219	0.309 084
$f_{2222}$	647.041 125	555.560 502	641.974 496	560.537 312
$f_{3311}$	1.414 079	2.727 029	1.260 871	2.119 260
$f_{3321}$	1.487 114	1.962 758	0.741 560	0.751 845
$f_{3322}$	0.536 898	2.941 737	0.264 920	1.448 129
$f_{3333}$	0.990 748	1.621 992	0.561 447	0.734 955

<sup>a</sup> See text for definitions of BLBA coordinates. Units are consistent with energy in aJ, bond lengths in Å, and angles in radians. There is also the additional relationship  $f_{3,3,3,3} = (f_{3333} + 4f_{33})/3$ .

CCSD(T)/cc-pVTZ *ab initio* data for the XNC species, where there is considerably less experimental data available for comparison.

Considering now the *ab initio* equilibrium geometries for the XNC species in Table 2, it is again found that improvement of the one-particle basis set from cc-pVDZ to cc-pVTZ substantially reduces the bond distances. In this case the Cl–N bond distance exhibits the largest effect, decreasing by  $\approx 0.024$  Å. To our knowledge, experimentally derived structures do not yet exist. On the basis of the results for the XCN species, however, and a recently published review of the accuracy of the CCSD(T)/spdf method for bond distances (including the HCN and HNC species),<sup>9</sup> it is expected that the CCSD(T)/cc-pVTZ approach will yield bond distances to a similar accuracy for XNC as for XCN. Comparison of the *ab initio* and experimental<sup>5</sup> fundamental frequencies for the two stretching modes of FNC and the CN stretch in CINC supports this assertion. These are the only fundamentals of the XNC species that are well-known experimentally, and the largest discrepancy here is only 14 cm<sup>-1</sup>. This is excellent agreement, especially considering that matrix effects may shift the experimental band centers somewhat. The Cl–N stretch, on the other hand, is predicted to occur at 702 cm<sup>-1</sup>, which clearly shows that the tentative assignment made at 615 cm<sup>-1</sup> is due to some other molecule. Hence the present study provides the first conclusive evidence that the 615 cm<sup>-1</sup> band observed in matrix isolation experiments<sup>5</sup> is not the Cl–N fundamental of CINC. Comparison of the present CCSD(T)/cc-pVTZ vibrational frequencies and force constants of FNC with the analogous CEPA values from ref 8 shows similar agreement to that found for FCN.

As the quartic force fields determined in this study are expected to be very accurate, they are presented in Table 3 in simple bond-length and bond-angle (BLBA) coordinates, also referred to as internal coordinates. The internal coordinate definitions are as follows:

$$S_1(\sigma) = r_1 \quad (1)$$

$$S_2(\sigma) = r_2 \quad (2)$$

$$S_3(\pi) = \rho = (180 - \alpha) \quad (3)$$

where  $r_1 = r_{XC}$  ( $r_{XN}$ ) for the XCN (XNC) species,  $r_2 = r_{CN}$ , and  $\alpha$  is the bond angle (i.e., 180° at equilibrium).

**TABLE 4: Symmetry Unique Force Constants (aJ) in Morse-Cosine Coordinates<sup>a</sup>**

	FCN	FNC	C1CN	C1NC
$F_3$	0.383 957	0.086 026	0.354 712	0.148 224
$F_{11}$	1.806 579	1.130 450	1.590 151	1.232 485
$F_{21}$	0.010 913	-0.102 274	0.027 153	-0.034 089
$F_{22}$	3.431 785	2.892 008	3.489 336	3.084 640
$F_{31}$	-0.287 013	-0.214 260	-0.304 348	-0.281 881
$F_{32}$	-0.575 009	-0.526 691	-0.381 012	-0.383 710
$F_{33}$	0.458 235	0.569 339	0.305 387	0.294 393
$F_{211}$	-0.162 608	-0.166 090	-0.170 187	-0.207 042
$F_{221}$	-0.027 830	0.017 236	0.004 141	0.016 885
$F_{311}$	-0.002 323	0.237 058	0.080 005	0.265 727
$F_{321}$	0.294 326	0.348 954	0.182 562	0.170 205
$F_{322}$	-0.470 547	0.035 150	-0.328 340	-0.096 492
$F_{1111}$	1.188 157	-0.283 963	0.966 449	0.003 650
$F_{2111}$	-0.209 826	-0.130 676	-0.249 081	-0.166 164
$F_{2211}$	-0.127 507	0.070 953	-0.156 784	-0.082 825
$F_{2221}$	-0.062 841	0.215 388	-0.073 672	0.098 621
$F_{2222}$	0.472 009	0.021 116	0.952 214	0.457 740

<sup>a</sup> See text for definitions of Morse-cosine coordinates.

As indicated previously, another purpose of the present study was to compare variational and perturbational approaches to obtaining fundamental vibrational frequencies. It is well-known that for accurate variational calculations it is necessary to represent the potential in a coordinate system that exhibits better asymptotic behavior than shown by BLBA coordinates. In this study we have used Morse-cosine coordinates for the variational calculations, and these are given below. The quartic force fields in Morse-cosine coordinates are given in Table 4. Note that force constants represented in BLBA coordinates are denoted by  $f$  whereas the force constants in Morse-cosine coordinates are denoted by  $F$ . The Morse-cosine coordinates are defined according to

$$S_1(\sigma) = 1 - \exp[-\gamma_1(r_1 - r_{10})] \quad (4)$$

$$S_2(\sigma) = 1 - \exp[-\gamma_2(r_2 - r_{20})] \quad (5)$$

$$S_3(\pi) = \cos(\alpha) - \cos(\alpha_0) = \cos(\alpha) + 1 \quad (6)$$

where  $\gamma_1 = -f_{111}/3f_{11}$ ,  $\gamma_2 = -f_{222}/3f_{22}$ , and  $r_{10}$  and  $r_{20}$  are the equilibrium values of  $r_1$  and  $r_2$ , respectively. Finally, in order to avoid confusion, we note that the force constants are given according to the following potential

$$V = V_0 + \frac{1}{2} \sum_{ij} f_{ij} \Delta S_i \Delta S_j + \frac{1}{6} \sum_{ijk} f_{ijk} \Delta S_i \Delta S_j \Delta S_k + \frac{1}{24} \sum_{ijkl} f_{ijkl} \Delta S_i \Delta S_j \Delta S_k \Delta S_l \quad (7)$$

and similarly for the  $F$  force constants.

**B. Comparison of Variational and Perturbational Fundamental Frequencies.** Table 5 contains a comparison of zero-point vibrational energies (ZPVE) and fundamental vibrational energies computed using variational and perturbational approaches. As is readily evident, the agreement between the variational and perturbational results is excellent. This is true even for  $\nu_2$  of C1CN, which is subject to a significant Fermi resonance with  $2\nu_3$ . The largest deviation is only 3  $\text{cm}^{-1}$  for the ZPVE of FCN, and the largest deviation for a fundamental is only 2  $\text{cm}^{-1}$ , which occurs for  $\nu_1$  and  $\nu_3$  of FNC. These comparisons are consistent with an earlier study<sup>27</sup> on HNO and DNO where it was also found that second-order perturbation theory and variation theory yield similar results (except for the H-N stretch in HNO, which is unusually anharmonic). These

**TABLE 5: Fundamental Vibrational Frequencies ( $\text{cm}^{-1}$ ) Determined from Second-Order Perturbation Theory and Exact Variational Calculations<sup>a</sup>**

	level	PT	variational	expt
FCN	ZPVE	2157	2154	
	$\nu_1$	2312	2312	2319
	$\nu_2$	1077	1076	1076
FNC	$\nu_3$	446	447	451
	ZPVE	1747	1748	
	$\nu_1$	2109	2111	2123
C1CN	$\nu_2$	935	935	928
	$\nu_3$	213	211	
	ZPVE	1863	1863	
C1NC	$\nu_1$	2209	2208	2216
	$\nu_2$	707	708	714
	$\nu_3$	379	379	379
C1NC	ZPVE	1635	1634	
	$\nu_1$	2069	2069	2074
	$\nu_2$	702	701	615?
	$\nu_3$	235	235	

<sup>a</sup> See the footnotes to Tables 1 and 2 for references to the experimental literature.

comparisons, together with the numerous second-order anharmonic studies by Martin, Lee, Taylor, and co-workers (for example, see refs 6 and 27–30 and references therein), in which very good agreement with experiment is obtained, demonstrate that before 1990 the major error in completely *ab initio* vibrational frequency calculations was usually due to deficiencies in the electronic structure method used to compute the potential function and not due to an inadequate treatment of the nuclear Schrödinger equation—even when second-order perturbation theory was used to solve the nuclear Schrödinger equation. These studies also serve to emphasize that *ab initio* electronic structure methods have progressed to the point where it is now possible to predict polyatomic fundamental vibrational frequencies that are often more accurate for the gas-phase species than values obtained from matrix isolation experiments. That is, shifts due to matrix effects are often larger than errors inherent in the current state-of-the-art *ab initio* calculation of vibrational frequencies. For example, Milligan and Jacox<sup>5</sup> have shown that the bending and C–H stretch fundamentals of HCN differ by 20–30  $\text{cm}^{-1}$ , depending on whether an Ar or N<sub>2</sub> matrix is used. Even in an Ar matrix the bending fundamental of HNC differs by 13  $\text{cm}^{-1}$  from the gas phase value.<sup>5,31</sup> Many examples showing that shifts due to matrix effects are often 20  $\text{cm}^{-1}$  or more are provided in the recent review by Jacox.<sup>32</sup> These examples also show that shifts in Ne matrices are generally much smaller than found in N<sub>2</sub>, Ar, or heavier noble gas atom matrices. It must, however, be emphasized that state-of-the-art *ab initio* methodology must be used in order to arrive at this conclusion, and this requires the use of a correlation method at least as sophisticated as CCSD(T) in conjunction with a one-particle basis set that contains at least  $f$  functions. Finally, it is also important to point out that state-of-the-art *ab initio* predictions of rovibrational spectra are now sufficiently accurate that they may be used to identify, interpret, or analyze a spectrum that is not from a tightly controlled laboratory environment (i.e., an environment in which unknown contaminants will be present such as a spectrum from interstellar dust).

**C. XCN and XNC Heats of Formation.** As indicated previously, another purpose of the present study is to determine accurate heats of formation of the FCN, FNC, C1CN, and C1NC molecules. In paper I the XCN  $\rightarrow$  XNC isomerization energies were accurately determined to be  $69.5 \pm 1.0$  and  $42.7 \pm 1.0$  kcal/mol for X = F and Cl, respectively, but these could not easily be put on an absolute scale. Results from the present study allow two methods to be used to determine heats of

formation of the FCN and ClCN species. The first approach is based on an empirical correction scheme for atomization energies devised by Martin.<sup>11</sup> In this approach Martin devised a three-term correction formula that depends on the change in the numbers of  $\sigma$  bonds,  $\pi$  bonds, and pairs of valence electrons in the atomization reaction. Correction factors for several different levels of theory, which are defined by both the electron correlation treatment and the one-particle basis set that is used, were determined by fitting to a set of molecules for which accurate experimental atomization energies are known. Note that the atomic heats of formation that were used refer to the lowest spin-orbit state or, in other words, the empirical correction scheme is designed to account for relativistic effects. The interested reader is referred to ref 11 for a more detailed account of this technique. The energies contained in Table 1 allow this approach to be applied to FCN and ClCN, and doing this we obtain 300.6 kcal/mol (cc-pVDZ), 303.8 kcal/mol (cc-pVTZ), and 304.4 kcal/mol (cc-pVQZ) for the atomization energy (0 K) of FCN (ClCN is discussed below). The results exhibit a good convergence. Taking the cc-pVQZ result as our best estimate, correcting it with the variational zero-point energy from Table 5, and combining this with the experimental<sup>10</sup> heats of formation for F, C, and N leads to a  $\Delta H_{f,0}^\circ(\text{FCN})$  of 2.7 kcal/mol, which is considerably different from the experimental<sup>10</sup> value of  $8.5 \pm 4$  kcal/mol. It is difficult to assign an uncertainty to the theoretical value (for the CCSD(T)/cc-pVQZ level of theory, Martin<sup>11</sup> obtained a mean absolute error of only 0.46 kcal/mol and a maximum error of 0.98 kcal/mol for the test molecules), but a very conservative estimate would be  $\pm 1.5$  kcal/mol, which indicates that the experimental heat of formation contains a substantial error.

Before discussing ClCN, we examine an alternative approach to determining  $\Delta H_{f,0}^\circ(\text{FCN})$ . Woon<sup>12</sup> has shown that results with the correlation consistent basis sets often exhibit an exponential convergence pattern. In other words, defining an atomization energy as  $E(\text{At})$ , we could write

$$E(\text{At}) = E(\text{At})_\infty + a \exp(-bn) \quad (8)$$

where  $E(\text{At})_\infty$  is the atomization energy at the one-particle basis set limit and  $n$  is the number of the basis set (i.e., cc-pVDZ has  $n = 1$ , cc-pVTZ has  $n = 2$ , etc.). Performing this extrapolation for the atomization of FCN, we obtain 303.1 kcal/mol for  $E(\text{At})_\infty$ . It should be kept in mind that this value is not directly comparable to the value obtained from Martin's scheme, since the empirical correction is designed to account for small effects such as core-correlation, spin-orbit splitting in the atoms, and higher-order correlation effects. The value obtained from eq 8 does not include any of these effects, but they may be estimated. The spin-orbit splitting of the atoms may be taken into account by using "nonrelativistic" (or spin-orbit-averaged) atomic heats of formation. This is easily done with knowledge of the spin-orbit splittings<sup>10</sup> and using  $\sum_j (2j + 1)E_j / \sum_j (2j + 1)$  to compute the "average" state. For the XCN and XNC species the major effect of core-correlation is due to dissociation of the CN bond, and Pradhan *et al.*<sup>33</sup> have recently shown that core-correlation increases the C-N dissociation energy by 1.18 kcal/mol. Applying this correction to the extrapolated value, including the zero-point energy from Table 5, and using the "averaged" atomic heats of formation as discussed above, we obtain a  $\Delta H_{f,0}^\circ(\text{FCN})$  value of 3.4 kcal/mol. This value is in excellent agreement with the value obtained from Martin's empirical scheme, 2.7 kcal/mol. For our best estimate of  $\Delta H_{f,0}^\circ(\text{FCN})$ , we average the two computed values, giving 3.1 kcal/mol, and assign the conservative uncertainty of  $\pm 1.5$  kcal/mol.

Applying the empirical scheme to ClCN, atomization energies

of 281.1 kcal/mol (cc-pVDZ), 282.1 kcal/mol (cc-pVTZ), and 283.1 kcal/mol (cc-pVQZ) are obtained. Again, taking the cc-pVQZ result as the best estimate and including the ClCN zero-point energy from Table 5, a  $\Delta H_{f,0}^\circ(\text{ClCN})$  value of 33.3 kcal/mol is obtained. Using the second approach described in this section, we obtain 33.1 kcal/mol for  $\Delta H_{f,0}^\circ(\text{ClCN})$ . These values are also in excellent agreement, and we take the average, 33.2 kcal/mol, as our best estimate and assign the conservative uncertainty of  $\pm 1.5$  kcal/mol. Our best estimate,  $33.2 \pm 1.5$  kcal/mol, is in very good agreement with the experimental value,<sup>10</sup> 32.8 kcal/mol. This lends confidence to the computed value for FCN.

Combining these best estimates with the isomerization energies reported in paper I, we obtain  $72.6 \pm 1.5$  and  $75.9 \pm 1.5$  kcal/mol for  $\Delta H_{f,0}^\circ(\text{FNC})$  and  $\Delta H_{f,0}^\circ(\text{ClNC})$ , respectively. It is concluded that the best available heats of formation for the FCN, FNC, and ClNC molecules are the best estimates given in this work.

## Conclusions

The equilibrium geometries, quartic force fields, and fundamental vibrational frequencies of FCN, FNC, ClCN, and ClNC have been computed using the CCSD(T) correlation method in conjunction with the cc-pVTZ one-particle basis set. Equilibrium geometries have also been determined for FCN and ClCN using the cc-pVQZ basis set, which includes g-type functions. Much of this data is not known from experiments, and it is expected that the highly accurate *ab initio* values will aid in the interpretation of future experiments. The theoretical predictions are in good agreement with the available experimental data with the exception of the Cl-C bond distance in ClCN and the tentatively assigned Cl-N stretching fundamental for ClNC. In both cases it is asserted that the experimentally derived data are in error.

The fundamental vibrational frequencies were computed using two different approaches for solving the nuclear Schrödinger equation, these being second-order perturbation theory and variation theory. Excellent agreement is found between the two approaches (and also with experiment, as indicated above) even for the Cl-C stretching fundamental of ClCN, which is in fairly strong Fermi resonance with the first overtone of the bending mode. It is important, however, that this Fermi resonance be treated properly in the perturbation theory in order to avoid the calculation of near-singular terms. On the basis of the results of this study and also of the results of several similar studies that we have performed in recent years,<sup>6,27-30</sup> it is concluded that state-of-the-art *ab initio* theory is often capable of predicting vibrational band centers of some gas-phase species more accurately than is possible from matrix isolation experiments. In other words, the shifts due to matrix effects are often larger than the errors inherent in current state-of-the-art *ab initio* predictions, especially when  $\text{N}_2$ , Ar, or heavier noble gas atoms are used as the matrix. It must be emphasized that state-of-the-art *ab initio* methodology must be used in order to arrive at this conclusion, and this requires the use of a correlation method at least as sophisticated as CCSD(T) in conjunction with a one-particle basis set that contains at least  $f$  functions.

Accurate heats of formation of the FCN, ClCN, FNC, and ClNC species ( $3.1 \pm 1.5$ ,  $33.2 \pm 1.5$ ,  $72.6 \pm 1.5$ , and  $75.9 \pm 1.5$  kcal/mol, respectively; all at 0 K) have also been determined. The reliability of these predictions is supported by the fact that two different approaches were used and yield results that are in excellent agreement. The theoretical prediction for the heat of formation of FCN does not agree with the currently accepted experimental value,<sup>10</sup> and it is concluded that the experimental

value is incorrect. The *ab initio* heat of formation of C1CN is in excellent agreement with the experimental value.

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