An ab Initio Study on the Equilibrium Structure and *X*CN Bending Energy Levels of Halofulminates: ClCNO

Jacek Koput*

Department of Chemistry, Adam Mickiewicz University, 60−780 Poznań, Poland

Received: December 3, 1998; In Final Form: January 18, 1999

The molecular parameters of chlorofulminate, ClCNO, were determined in large-scale ab initio calculations using the coupled-cluster method, CCSD(T), and basis sets of double- through quintuple-zeta quality. With the largest basis set employed, the equilibrium structure of the molecule was found to be bent, with the parameters r(ClC) = 1.6490 Å, r(CN) = 1.1749 Å, r(NO) = 1.2039 Å, ∠(ClCN) = 152.22°, and ∠(NCO) = 171.50°. The potential energy function for the large-amplitude ClCN bending motion (the ν_5 mode) was determined to be strongly anharmonic, with a barrier to linearity of the ClCNO chain of 156 cm^{-1}. The rotation−bending energy levels were then calculated using a semirigid-bender Hamiltonian. The effective rotational constants determined for various ν_5 states were found to be in excellent agreement with the recent experimental data.

1. Introduction

Halofulminates, *X*CNO (where *X* = F, Cl, Br, or I), are highly reactive, short-lived derivatives of fulminic acid, HCNO. The parent species is well known as the prominent example of a quasilinear molecule.[1] The fulminic acid molecule was found both experimentally[2] and theoretically[3] to be very nearly linear at equilibrium, with a barrier to linearity of the HCNO chain of only a few centimeters^{-1}. The potential energy function for the HCN bending mode, ν_5, was determined to be strongly anharmonic and extraordinarily flat in the vicinity of the minimum. The shape of the potential energy function results in a large amplitude of the HCN bending motion, calculated to be 34° for the ground vibrational state.[2] It results also in an unusual dependence of the rotational constants upon excitation of the HCN bending mode, which resembles neither the regular dependence characteristic of a rigid linear-chain molecule nor that of a rigid asymmetric-top molecule. In view of a large amplitude of the HCN bending motion, interpretation of the structure and rotation−vibration spectra of fulminic acid requires an explicit model of the quasilinear dynamics.

Recently, the rotational spectra of two halofulminates, BrCNO and ClCNO, were measured and analyzed.[4,5] The spectra of both molecules were observed to be very dense and complex because of a large number of intense vibrational satellites. In analogy to fulminic acid, the observed lines were assigned to the *a*-type *R*-branch rotational transitions arising from molecules in various excited states of the lowest-frequency vibrational mode ν_5, which is predominantly the BrCN/ClCN bending mode. The assignments of the vibrational quantum numbers, v_5 and l_5 in terms of the linear-molecule model, were made on the basis of relative line intensities, *l*-type resonance splittings, and Br/Cl nuclear quadrupole splittings. The patterns of the rotational spectra are even more irregular than that found for fulminic acid, thus clearly indicating quasilinearity of the *X*CNO chain for both the BrCNO and ClCNO molecules.

To assist in a further analysis of the rotational spectra of halofulminates, large-scale ab initio calculations on the equilibrium structures and *X*CN bending potential energy functions of the FCNO, ClCNO, and BrCNO molecules were performed. The molecular properties were determined by the coupled-cluster (CC) method[6,7] with large one-particle basis sets, up to *spdfgh* quality. The potential energy functions thus determined were used to calculate the rotation−bending energy levels and effective rotational constants in various states of the *X*CN bending mode. In this paper, the results of calculations for chlorofulminate, ClCNO, are reported. The results for fluoro- and bromofulminate will be reported elsewhere.

To the author's knowledge, the most advanced ab initio study on chlorofulminate was that performed recently by Pasinszki and Westwood.[8] The structure of the molecule and a barrier to linearity of the ClCNO chain were determined using several quantum-mechanical methods, ranging from self-consistent field (SCF) to CC, and the split-valence 6−31G(d) or 6−311G(2d) basis sets. Some calculations at lower levels of theory were also performed with the correlation-consistent cc-pVTZ basis set. The equilibrium structure of the ClCNO molecule was predicted to be either linear or bent depending on the method and one-particle basis set employed. The predicted height of the barrier to linearity of the ClCNO chain ranged from 0 to 1266 cm^{-1}. The large sensitivity of the results to the level of theory resembles closely that observed for the HCNO molecule.[9] It was therefore to be expected that reliable results on the molecular parameters of chlorofulminate, as in the case of the parent acid,[3] could only be obtained using extensively correlated electronic wave functions in conjunction with large one-particle basis sets.

2. Method of Calculation

The molecular parameters of chlorofulminate were calculated using the CC method including single and double excitations and a perturbational correction due to connected triple excitations, CCSD(T).[10,11] The basis sets used in this study are the correlation-consistent polarized basis sets, cc-pV*n*Z.[12,13] The quality of the basis sets employed ranges from double zeta (*n*

---

* Address for correspondence. Department of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60−780 Poznań, Poland. E-mail: koput@amu.edu.pl.

10.1021/jp984600k CCC: $18.00

TABLE 1: Equilibrium Molecular Parameters of Chlorofulminate, Determined Using the CCSD(T) Method and Various cc-pV*n*Z Basis Sets

	cc-pVDZ	cc-pVTZ	cc-pVQZ	Q/5[a]
r(ClC) (Å)	1.6882	1.6614	1.6523	1.6490
r(CN) (Å)	1.2063	1.1813	1.1747	1.1749
r(NO) (Å)	1.2060	1.2048	1.2040	1.2039
∠(ClCN) (deg)	142.01	149.83	152.18	152.22
∠(CNO) (deg)	167.59	170.60	171.50	171.50
energy + 627 (hartree)	−0.198414	−0.435289	−0.509647	−0.517945

[a] cc-pV5Z for chlorine, cc-pVQZ for the other atoms.

= D), through triple zeta (*n* = T), to quadruple zeta (*n* = Q). To investigate further the effects of extension of the one-particle basis set, final calculations were performed using the quintuple-zeta basis set, cc-pV5Z, for chlorine and the cc-pVQZ basis set for the other atoms. This basis set is referred to hereafter as Q/5. The cc-pV*n*Z functions provide a systematic way of enlarging the basis set. The accuracy of the results obtained with increasing quality of the basis set can thus be conveniently estimated, assuming monotonic convergence of the calculated properties toward the limit of an infinite basis set. The largest basis set employed, Q/5, consists of a (20s12p4d3f2g1h)/[7s6p4d3f2g1h] set for chlorine and a (12s6p3d2f1g)/[5s4p3d2f1g] set for carbon, nitrogen, and oxygen, thus resulting in a molecular one-particle basis set of 260 contracted functions. Only the spherical harmonic components of polarization *d* through *h* functions were used. In the correlation treatment, the 1*s*- and 2*sp*-like core orbitals of chlorine and 1*s*-like core orbitals of the other atoms were excluded from the active space.

The ab initio calculations were performed using the MOLPRO-96 program.[14,15]

The energy levels of the ClCN bending motion and rotation of the ClCNO molecule were calculated using the semirigid-bender model.[2,16] In this model, the rotation−vibration energy levels of a nonrigid *WXYZ* molecule can be related directly to the structural parameters and shape of the potential energy surface. The energy levels and wave functions are calculated using an approximate four-dimensional Hamiltonian, which describes a *WXYZ* molecule bending at the *WXY* angle and rotating in space. The quantities appearing in the Hamiltonian are functions of the *WXY* bending coordinate; they depend as well on the structural and bending potential function parameters. All other vibrations of the molecule are assumed to be of small amplitude. Interaction of the *WXY* bending motion with the other vibrational degrees of freedom is accounted for by varying the structural parameters along the minimum-energy bending potential function. The rotation−bending energy levels are calculated variationally by diagonalizing the Hamiltonian matrix in a basis set consisting of products of rotational symmetric-top and *WXY* bending wave functions.

3. Results and Discussion

The calculated equilibrium molecular parameters of chlorofulminate are given in Table 1. For all the basis sets employed, the equilibrium structure of the molecule was found to be planar and bent, with the trans conformation of the ClCNO chain. The calculated values appear to converge with enlargment of the one-particle basis set. The largest improvement occurs for the valence angle ClCN. Extension of the basis set for chlorine alone, from cc-pVQZ to cc-pV5Z (column heading Q/5), affects substantially only the ClC bond length, while (surprisingly) it does not influence the valence angle ClCN. For the cc-pV5Z basis set for all the atoms, changes in the molecular parameters can be estimated assuming that the incremental changes in the parameters follow a geometric series.[12] Extension from the cc-pVQZ to cc-pV5Z basis set would thus lower the total energy by ≈23 millihartrees, nearly three times larger than the energy lowering determined for the Q/5 basis set. The total energy lowering at the limit of the infinite basis set could be estimated to be ≈34 millihartrees. Likewise, extension from the cc-pVQZ to cc-pV5Z basis set would shorten the ClC, CN, and NO bond lengths by about 0.0031, 0.0017, and 0.0005 Å, respectively. The valence angles in ClCN and CNO would widen by about 0.71 and 0.27°, respectively. It is interesting to compare the predicted changes in the structural parameters with those determined by extending the basis set for chlorine only. On going from the cc-pVQZ to Q/5 basis set, the calculated ClC bond length decreases by 0.0033 Å, nearly by the amount predicted with geometric-series extrapolation. The other structural parameters change to a much smaller extent, indicating that the predicted changes would be largely due to extension of the one-particle basis set for the carbon, nitrogen, and oxygen atoms.

TABLE 2: Molecular Parameters of the Linear Configuration of Chlorofulminate, Determined Using the CCSD(T) Method and Various cc-pV*n*Z Basis Sets

	cc-pVDZ	cc-pVTZ	cc-pVQZ	Q/5[a]
r(ClC) (Å)	1.6618	1.6442	1.6377	1.6345
r(CN) (Å)	1.1795	1.1649	1.1610	1.1612
r(NO) (Å)	1.2153	1.2121	1.2104	1.2103
ΔE^b (cm^{-1})	796	238	159	156

[a] cc-pV5Z for chlorine, cc-pVQZ for the other atoms. [b] ΔE is the energy difference between the linear and equilibrium structures.

TABLE 3: Optimized Values of the Structural Parameters[a] of Chlorofulminate, Determined for Various Assumed Values of the ClCN Angle Using the CCSD(T) Method

r(ClC) (Å)	1.6377	1.6396	1.6453	1.6523	1.6682
r(CN) (Å)	1.1610	1.1628	1.1683	1.1747	1.1876
r(NO) (Å)	1.2104	1.2095	1.2068	1.2040	1.1989
∠(ClCN) (deg)	180.0	170.0	160.0	152.18	140.0
∠(CNO) (deg)	180.0	176.82	173.75	171.50	168.43
energy (cm^{-1})^{b,a}	0	−37.5	−120.5	−158.7	22.8
energy (cm^{-1})^{b,c}	0	−37.1	−119.0	−156.0	26.8

[a] Calculated with the cc-pVQZ basis set. [b] Relative to the energy of the linear configuration. [c] Calculated with the Q/5 basis set.

Table 2 lists the molecular parameters calculated for the linear configuration of the chlorofulminate molecule. As for the equilibrium configuration, the molecular parameters converge monotonically with the increasing size of the one-particle basis set. The calculated barrier to linearity of the ClCNO chain changes substantially, with the barrier height decreasing by about a factor of 5 on going from the cc-pVDZ to cc-pVQZ basis set. For the cc-pV5Z basis set for all of the atoms, the barrier to linearity would be lower by about 11 cm^{-1} than that determined with the cc-pVQZ basis set. Extension of the basis set for the chlorine atom alone lowers the barrier to linearity by only 3 cm^{-1}.

The ClCN bending potential energy function was determined by optimizing the structural parameters for various assumed values of the ClCN angle. Results of the calculations with the cc-pVQZ and Q/5 basis sets are given in Table 3. Because the height of the barrier to linearity was determined to differ by only 3 cm^{-1} for both basis sets (compare Table 2), the structural parameters were optimized using the cc-pVQZ basis set only. Then, the total energy was calculated for each structure using the Q/5 basis set. As was found for the barrier to linearity, the shape of the ClCN bending potential function was determined

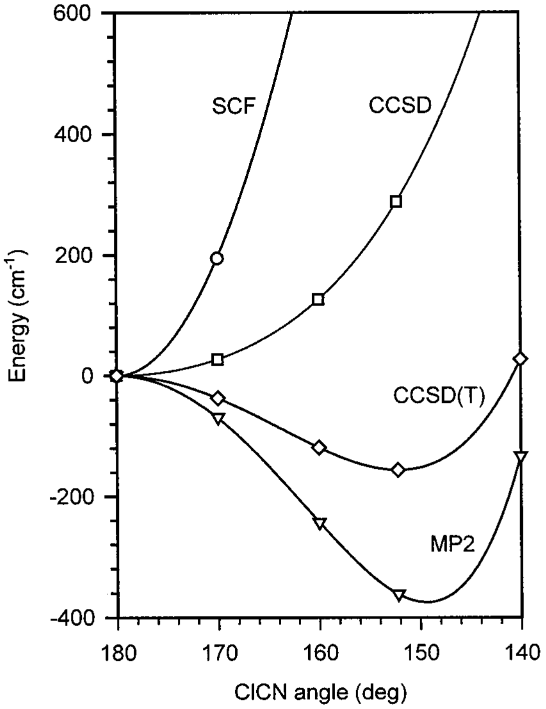

Figure 1. The (relative) total energy of chlorofulminate as a function of the ClCN angle, determined using the Q/5 basis set at the SCF, MP2, CCSD, and CCSD(T) levels of theory. The functions are drawn to a common scale.

TABLE 4: The Total Energy[a] of Chlorofulminate (in cm^{-1}) as a Function of the ClCN Angle, Determined Using the Q/5 Basis Set at Various Levels of Theory

∠(ClCN)	180	170	160	152.18	140
SCF	0	194.7	769.9	1444.1	2791.7
MP2	0	−68.9	−243.2	−361.3	−133.0
CCSD	0	27.0	126.6	288.0	806.8
CCSD(T)	0	−37.1	−119.0	−156.0	26.8
CCSD+T(CCSD)	0	−49.4	−161.1	−223.2	−74.8
CCSD−T	0	−35.3	−113.9	−149.7	27.4

[a] Relative to the energy of the linear configuration, calculated with the structural parameters given in Table 3.

to be essentially the same for both basis sets. The differences in the calculated total energies amount to at most 4 cm^{-1}. All of the structural parameters are found to vary significantly with the ClCN angle. The ClC and CN bond lengths increase, while the NO bond length decreases nonlinearly with the decreasing ClCN angle. The differences amount to as much as 0.03 Å when the ClCN angle ranges from 180 to 140°. The valence angle CNO also changes substantially, with the difference amounting to about 12°.

To investigate the effect of electron correlation on the shape of the ClCN bending potential energy function, the calculations were performed at various levels of theory, namely SCF,[17] second-order Møller−Plesset (MP2),[18] and CC.[6,7] Within the CC method, the effect of connected triple excitations was accounted for by employing the CCSD(T),[10,11] CCSD+T(CCSD),[19] and CCSD-T[20] approaches. The calculations were performed using the one-particle Q/5 basis set and the structural parameters given in Table 3. The potential energy functions thus determined are shown in Figure 1 and are also presented in Table 4. The shape of the ClCN bending potential energy function is due to a balance among different electron correlation effects. At the SCF level, the ClCNO chain is predicted to be linear at equilibrium. Inclusion of the effect of double excitations within the perturbational MP2 approach favors the bent configuration, with a minimum at the ClCN angle of about 149° and a barrier to linearity of the ClCNO chain of 375 cm^{-1}. Inclusion of the effects of connected single and double excitations through the CCSD framework results again in a linear configuration. However, upon inclusion of the effect of connected triple excitations, the equilibrium structure of the ClCNO molecule is predicted, in turn, to be bent. The changes in the shape of the ClCN bending potential energy function upon inclusion of different correlation effects resemble closely those found previously for the parent acid, the HCNO molecule.[3] A comparison of the potential energy functions calculated with different approximate treatments of connected triple excitations is presented in Table 4. The CCSD(T) and CCSD-T methods yield essentially the same results, whereas the effect of triple excitations seems to be overestimated by the CCSD+T(CCSD) method. A conclusive answer to the role of connected higher-than-double excitations calls for calculations with the CCSDT and (perhaps) CCSDTQ methods and large one-particle basis sets.

To characterize further the ClCN bending potential energy function, the calculated total energies were fitted with an analytical function. A quadratic potential with a Lorentzian hump was chosen here,

$$V(\rho) = \frac{Hf(\rho^2 - \rho_e^2)^2}{f\rho_e^4 + (8H - f\rho_e^2)\rho^2} \tag{1}$$

where ρ is the supplement of the ClCN angle, ρ_e is the equilibrium angle, H is the height of a barrier to linearity of the ClCNO chain, and f is the harmonic force constant at $\rho = \rho_e$. The parameters were adjusted in a least-squares fit of eq 1 to the total energies calculated with the Q/5 basis set (Table 3). The root-mean-square deviation of the fit is about 0.1 cm^{-1}, and the parameters are determined to be $H = 156.0$ cm^{-1}, $\rho_e = 27.87°$, and $f = 0.1070$ mdyn Å.

The ClCN bending potential energy function thus determined was used to calculate the rotation−bending energy levels of chlorofulminate. The energy levels and wave functions were calculated using an approximate, semirigid-bender Hamiltonian.[2,16] The quantities appearing in the Hamiltonian are assumed to be functions of the coordinate of the large-amplitude ClCN bending motion ρ. Therefore, the calculated structural parameters of the ClCNO molecule were expanded as polynomials in ρ. From the results quoted above, the expansions were determined to be

$$\begin{aligned} r(\mathrm{ClC}) &= 1.6345 + 0.06152\rho^2 + 0.00205\rho^4 \\ r(\mathrm{CN}) &= 1.1612 + 0.06165\rho^2 - 0.01442\rho^4 \\ r(\mathrm{NO}) &= 1.2103 - 0.03082\rho^2 + 0.01485\rho^4 \\ \gamma &= 18.357\rho - 3.657\rho^3 \end{aligned} \tag{2}$$

where ρ is given in radians, the bond lengths in Angstroms, and the supplement of the valence angle CNO, γ, in degrees. The energy levels and wave functions are labeled by symmetry labels and the rotational (J, k) and ClCN bending (n) quantum numbers. k is the quantum number for a component of the rotational angular momentum along the molecule-fixed a axis ($|k| = K_a$). The quantum number n is the number of nodes in a ClCN bending wave function over the range $(0, \pi)$. The quantum numbers n and k can be related to the vibrational quantum numbers v_5 and l_5 used in the standard approach[21] to describe

TABLE 5: $J = |l_5|$ Rotation−Bending Energy Levels (in cm^{-1}) and Changes in the Effective Rotational Constant B (in MHz) Due to Excitation of the ClCN Bending Mode, ν_5, of Chlorofulminate

$v_5^{l_5}$	energy[a]	ΔB (calc.)[b]	ΔB (exp.)[b,c]
0^0	0.0	0.0	0.0000
1^1	20.3	4.7	3.5157
1^1	20.3	14.6	13.9945
2^2	62.4	20.2	18.9884
3^3	119.8	30.6	29.2067
2^0	125.3	−7.0	−7.3696
3^1	180.3	7.1	6.7345
3^1	180.3	17.5	18.1275
4^4	189.3	40.6	39.1622
4^2	247.7	26.2	26.6182
5^5	268.9	50.2	48.8275
4^0	276.4	13.8	12.6601
5^3	325.3	38.1	38.7153
6^6	357.0	59.5	58.2241
5^1	362.4	20.4	20.1813
5^1	362.4	32.9	34.0185
6^4	411.6	49.0	49.6913
6^2	452.1	38.7	39.9182
6^0	468.2	33.3	33.7667

[a] The ground-state energy level is calculated to lie 65.3 cm^{-1} above the minimum of the potential energy function. [b] Calculated and experimental ground-state effective rotational constants B are 2567.3 and 2572.7818 MHz, respectively. [c] From an analysis of the micro- and millimeter wave spectra, ref 5.

the doubly-degenerate WXY bending mode ν_5 of a rigid linear-chain $WXYZ$ molecule. These relations are: $v_5 = 2n + |k|$ and $l_5 = k$.

The calculated $J = |k|$ rotation−bending energy levels of the main isotopic species of chlorofulminate are listed in Table 5. For the sake of comparison with the experimental data,[4,5] the energy levels are labeled with the quantum numbers v_5 and l_5. The location of the energy levels relative to the ClCN bending potential energy function is shown in Figure 2. The energy levels labeled with the same ClCN bending quantum number n are shown as separate stacks, each stack beginning with the rotationless $(J = 0)$ level. As for a prolate top, the energy increases with the increasing rotational quantum number k within each stack. The ground vibrational state, $n = 0$, is calculated to lie 91 cm^{-1} below the top of a barrier to linearity of the ClCNO chain, whereas the first excited ClCN bending state, $n = 1$, is located 35 cm^{-1} above the top of the barrier. For the ground state, the classical turning points for the ClCN bending motion are determined to lie at the valence angle ClCN of 144 and 163°. The amplitude of the ClCN bending motion increases twice in the first excited state, covering a substantial range of about 40°. Although transitions between the ClCN bending energy levels have not been observed experimentally so far, the relative energy of the $v_5^{l_5} = 1^1$ state can be estimated using the spectroscopic constants determined in an analysis of the rotational spectra of chlorofulminate. The $1^1 - 0^0$ energy level separation is estimated in this way[5] to be 24 ± 6 cm^{-1}. The predicted ab initio value of 20.3 cm^{-1} falls well within the experimental error bars.

The calculated rotation−bending energy levels were then used to determine the effective rotational constant B for each vibrational $v_5^{l_5}$ state. The corresponding values were obtained by fitting an odd power series in $(J + 1)$ to the calculated rotational transition energies.[21] The effective rotational constant B for the ground vibrational state of the main isotopic species of chlorofulminate is determined in this way to be 2567.3 MHz. The predicted value is in excellent agreement with the experimental value of 2572.7818 MHz.[5] The rotational constant B changes substantially and, for many energy levels, irregularly with excitation of the ClCN bending mode. The observed pattern of the rotational constants is highly anomalous.[5] In particular, the rotational constant B for the excited $v_5^{l_5} = 2^0$ state was found to be smaller than that of the ground vibrational state. The predicted and observed changes are listed in Table 5. The ab initio and experimental values agree to within about ±1 MHz for 18 excited energy levels ranging up to nearly 500 cm^{-1} above the ground state. The agreement between the theoretical and experimental data is suspiciously excellent, suggesting that the errors inherent in the ab initio methods (a limited one-particle basis set, some neglected correlation effects) may partly compensate for the neglected effects of the small-amplitude vibrations in the calculation of the rotation−bending energy levels. Nevertheless, the molecular parameters of chlorofulminate, especially the ClCN bending potential energy function, are predicted quite satisfactorily. We consider the agreement between the predicted and observed changes in the effective rotational constant B to be a strong confirmation of the validity of the calculations.

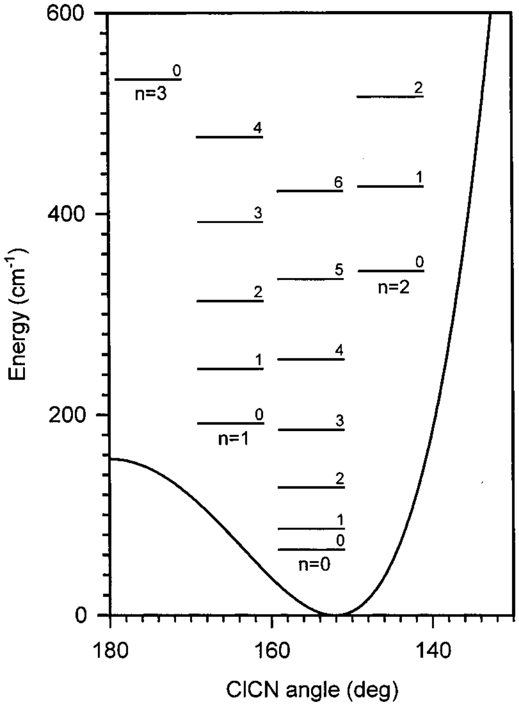

Figure 2. The calculated ClCN bending potential energy function and location of the lowest $J = |k|$ rotation−bending energy levels of chlorofulminate. Various stacks of the energy levels are shown schematically, each labeled by the ClCN bending quantum number n. Within each stack; the energy levels are labeled by the rotational quantum number k.

Changes in the effective rotational constant B for the rotationless ClCN bending states ($v_5^{l_5} = 0^0, 2^0, 4^0, 6^0$, ...) can be qualitatively attributed to effective shortening or elongation of the ClCNO molecule along the long axis (the molecule-fixed a axis). Upon excitation of the ClCN bending mode, the corresponding wave function spreads over a large range of the ClCN bending coordinate ρ. Depending on the shape of the potential energy function, it extends toward small or large values of ρ. The ClCN bending potential energy function rises less steeply on the barrier side. Therefore, on going from the $n = 0$ (0^0) to $n = 1$ (2^0) state, the wave function extends to smaller values of ρ, leading to an effective elongation of the ClCNO molecule and thus to a smaller rotational constant B. All of the excited rotationless ClCN bending states lie above the top of a barrier to linearity of the ClCNO chain. Therefore, on going from the $n = 1$ (2^0) to $n = 2$ (4^0) state, the wave function extends to larger values of ρ, leading to an effective shortening of the ClCNO molecule and thus to a larger rotational constant B. This is also the case for the higher excited ClCN bending states.

To quantify quasilinearity of the ClCNO chain, the parameter γ_0 can be calculated, ranging from -1 for an ideal linear molecule to $+1$ for an ideal bent molecule.[1,22] From the calculated rotation−bending energy levels of chlorofulminate, the parameter γ_0 is determined to be 0.35. For the parent acid, the HCNO molecule, the parameter γ_0 is determined to be −0.66.[2]

In conclusion, the ClCNO molecule is shown clearly to be another prominent example of a quasilinear molecule. The state-of-the-art ab initio methods are shown to be applicable for reliably predicting the electronic structure and unusual vibrational dynamics of such species.

Acknowledgment. The author is grateful to H. Lichau, B. P. Winnewisser, and M. Winnewisser for providing the results of their studies prior to publication and for stimulating discussions and comments.

References and Notes

(1) Winnewisser, B. P. in *Molecular Spectroscopy−Modern Research;* Narahari Rao, K. Ed.; Academic Press, Orlando, 1985; Vol. 3.

(2) Bunker, P. R.; Landsberg, B. M.; Winnewisser, B. P. *J. Mol. Spectrosc.* **1979**, 74, 9.

(3) Koput, J.; Winnewisser, B. P.; Winnewisser, M. *Chem. Phys. Lett.* **1996**, *255*, 357, and references therein.

(4) Gillies, C. W.; Gillies, J. Z.; Lichau, H.; Winnewisser, B. P.; Winnewisser, M. *Chem. Phys. Lett.* **1998**, *285*, 391.

(5) Lichau, H.; Winnewisser, B. P.; Winnewisser, M.; Gillies, C. W.; Gillies, J. Z. private communication, to be submitted for publication.

(6) Čižek, J. *J. Chem. Phys.* **1966**, 45, 4256.

(7) Purvis, G. D., III; Bartlett, R. J. *J. Chem. Phys.* **1982**, 76, 1910.

(8) Pasinszki, T.; Westwood, N. P. C. *J. Phys. Chem. A* **1998**, *102*, 4939.

(9) Handy, N. C.; Murray, C. W.; Amos, R. C. *Philos. Mag. B* **1994**, *69*, 755, and references therein.

(10) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, A. *Chem. Phys. Lett.* **1989**, *157*, 479.

(11) Scuseria, G. E.; Lee, T. J. *J. Chem. Phys.* **1990**, *93*, 5851.

(12) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(13) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358.

(14) MOLPRO-96 is a package of ab initio programs written by H.-J. Werner and P. J. Knowles, with contributions from J. Almlöf, R. D. Amos, M. J. O. Deegan, S. T. Elbert, C. Hampel, W. Meyer, K. A. Peterson, R. Pitzer, A. J. Stone, P. R. Taylor, R. Lindh, M. E. Mura, and T. Thorsteinsson.

(15) Hampel, C.; Peterson, K. A.; Werner, H.-J. *Chem. Phys. Lett.* **1992**, *190*, 1.

(16) Bunker, P. R.; Landsberg, B. M. *J. Mol. Spectrosc.* **1977**, 67, 374.

(17) Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69.

(18) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(19) Urban, M.; Noga, J.; Cole, S. J.; Bartlett, R. J. *J. Chem. Phys.* **1985**, *83*, 4041.

(20) Deegan, M. J. O.; Knowles, P. J. *Chem. Phys. Lett.* **1994**, *227*, 321.

(21) Papoušek, D.; Aliev, M. R. *Molecular Vibrational Rotational Spectra;* Academia, Prague, 1982.

(22) Yamada, K.; Winnewisser, M. *Z. Naturforsch. A* **1976**, *31*, 139.