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Ab Initio Study on the Equilibrium Structure and XCN Bending Energy Levels of Halofulminates: BrCNO

Jacek Koput*

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

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The molecular parameters of bromofulminate, BrCNO, have been determined in large-scale ab initio calculations using the coupled-cluster method, CCSD(T), and basis sets of double- through quintuple-ζ quality. The equilibrium structure of the molecule was found to be planar and bent, with the trans conformation of the BrCNO chain and the parameters $r(\text{BrC}) = 1.8043$ Å, $r(\text{CN}) = 1.1732$ Å, $r(\text{NO}) = 1.2036$ Å, $\angle(\text{BrCN}) = 153.09°$, $\angle(\text{NCO}) = 172.97°$. The potential energy function for the large-amplitude BrCN bending motion (the ν_5 mode) was determined to be strongly anharmonic, with a barrier to linearity of the BrCNO chain of 119 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

The very recent observation of the rotational spectra of two halofulminates, BrCNO and ClCNO,[1,2] indicates that the molecules are nonrigid. The patterns of vibrational satellites in the rotational spectra are even more irregular than that found for the parent acid, HCNO,[3] the molecule performing the large-amplitude HCN bending motion. The patterns observed for the BrCNO and ClCNO molecules are very similar and consistent with that characteristic of a quasi-linear molecule. Therefore, both molecules are expected[1,2] to undergo the large-amplitude BrCN/ClCN bending motion, with a low barrier to linearity of the BrCNO/ClCNO chain.

As the shape of a potential energy surface and location of the energy levels of a large-amplitude motion are keys to understanding the dynamics of any nonrigid molecule, large-scale ab initio calculations on halofulminates have been performed. In the previous paper,[4] the results for chlorofulminate were reported. It was shown that using the coupled-cluster (CC) method[5,6] in conjuction with the one-particle basis set of *spdfgh* quality, the ClCN bending potential energy function and the associated rotation-bending energy levels could be predicted with high accuracy. The chlorofulminate molecule was found to be indeed quasi-linear, with the barrier to linearity of the ClCNO chain of only 156 cm^{-1}. Experimentally observed changes[1,2] in the effective rotational constant B due to excitation of the ClCN bending mode were reproduced to within about ±1 MHz for 18 excited energy levels ranging up to nearly 500 cm^{-1} above the ground state. This work is an extension of the previous study,[4] and the results of analogous calculations for bromofulminate are reported. The results for another halofulminate, FCNO, will be reported elsewhere.[7]

To the author's knowledge, the most advanced ab initio study on bromofulminate is that performed by Pasinszki and Westwood.[8] The structure of the molecule and a barrier to linearity of the BrCNO chain were determined using several quantum-mechanical methods, ranging from self-consistent field to coupled-cluster, and the split-valence 6-31G(d) basis set. The equilibrium structure of the BrCNO molecule was predicted to be either linear or bent, depending on the method employed. The predicted height of the barrier to linearity of the BrCNO chain ranged from 0 to 759 cm^{-1}. The sensitivity of the results to the level of theory resembled closely that observed for the HCNO molecule.[9] Pasinszki and Westwood[8] came to believe that "we cannot, on the basis of the present calculations on the bromo analogue, draw any definitive conclusions on a linear or bent structure" and that bromofulminate has "probably a linear or quasi-linear structure". From results of the previous studies on the parent acid[10] and chlorofulminate,[4] it was to be expected that reliable results on the molecular parameters of bromofulminate could only be obtained using extensively correlated electronic wave functions calculated with large one-particle basis sets. Complete-basis-set limits for the calculated molecular parameters were estimated there using a sequence of the correlation-consistent polarized valence basis sets.[11] By employing the one-particle basis sets nearly saturated in both the valence and polarization spaces, it was possible to assess capability of different theoretical methods for accurately determining potential energy functions of the quasi-linear molecules in question.

2. Method of Calculation

The molecular parameters of bromofulminate were calculated using the coupled-cluster method including single and double excitations and a perturbational correction due to connected triple excitations, CCSD(T).[12,13] The one-particle basis sets employed are the correlation-consistent basis sets, cc-pVnZ.[11,14] The quality of the basis sets ranges from double ζ (n = D), through triple ζ (n = T), to quadruple ζ (n = Q). To investigate further the effects of extension of the one-particle basis set, final calculations were performed using the quintuple-ζ basis set, cc-pV5Z, for bromine and the cc-pVQZ basis set for the other atoms. This largest basis set employed here is referred to hereafter as Q/5. It consists of a (26s17p13d3f2g1h)/[8s7p5d3f2g1h]set for bromine and a (12s6p3d2f1g)/[5s4p3d2f1g] set for carbon, nitrogen, and oxygen, thus resulting in a molecular one-particle basis set of 269 contracted functions. Only the

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* E-mail: koput@amu.edu.pl.

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

	cc-pVDZ	cc-pVTZ	cc-pVQZ	Q/5[a]
r(BrC) (Å)	1.8379	1.8118	1.8050	1.8043
r(CN) (Å)	1.2036	1.1789	1.1732	1.1732
r(NO) (Å)	1.2059	1.2048	1.2037	1.2036
∠(BrCN) (deg)	143.66	152.96	154.80	154.53
∠(CNO) (deg)	169.23	172.37	173.04	172.97
energy + 2740 (hartree)	−0.062801	−0.352776	−0.424163	−0.430658

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

spherical harmonic components of polarization *d* through *h* functions were used. In the correlation treatment, the 1*s*-, 2*sp*-, and 3*spd*-like core orbitals of bromine and 1*s*-like core orbitals of the other atoms were excluded from the active space.

Since the relativistic effects were expected to be important for a bromine-containing molecule, expectation values of the mass−velocity and one-electron Darwin contact term integrals[15] were determined. These calculations were performed at the self-consistent field (SCF)[16] and complete active space self-consistent field (CASSCF)[17] levels of theory using the Q/5 basis set.[18] Bearing in mind the form of the Cowan−Griffin perturbation operator,[15] it would be desirable to determine the relativistic corrections with a one-particle basis set more accurate and flexible than cc-pV5Z in the vicinity of the bromine nucleus. However, due to the actual size of the molecular one-particle basis set such calculations appeared not to be practically feasible. In the CASSCF calculations, the electronic wave function consisted of a full valence complete active space. The wave function included thus all excitations of 22 valence electrons in 16 molecular orbitals corresponding to the valence atomic *sp* orbitals of the Br, C, N, and O atoms. Due to an extremely large number of excited configurations, the dynamic correlation effects on the calculated relativistic energy could not be estimated (through the multireference configuration interaction framework).

The ab initio calculations were performed using the MOLPRO-96 program.[19,20]

The energy levels of the BrCN bending motion and rotation of the BrCNO molecule were calculated using the semirigid-bender model.[21] The model was described at length previously[4] and the reader is referred to refs 21 and 3 for further details.

3. Results and Discussion

The calculated equilibrium molecular parameters of bromofulminate are given in Table 1. As for chlorofulminate,[4] the equilibrium structure of the bromofulminate molecule was found to be planar and bent, with the trans conformation of the BrCNO chain. As can be seen, the calculated values appear to converge with enlargment of the one-particle basis set. The largest improvement occurs for the valence angle BrCN. Extension of the basis set for bromine alone, from cc-pVQZ to cc-pV5Z (column headed Q/5), affects noticeably only the BrC bond length and the valence angle BrCN. 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.[11] Extension from the cc-pVQZ to cc-pV5Z basis set would thus lower the total energy by ≈18 millihartrees, thus 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 ≈23 millihartrees. Likewise, extension from the cc-pVQZ to cc-pV5Z basis set would shorten the BrC, CN, and NO bond lengths by about 0.0018, 0.0013, and 0.0011 Å, respectively. The valence angles BrCN and CNO would widen by about 0.36° and 0.14°, respectively. It is interesting to compare the predicted changes in the structural parameters with those determined by extending the basis set for bromine only. On going from the cc-pVQZ to Q/5 basis set, the calculated BrC bond length decreases by 0.0007 Å, nearly half of the amount predicted with geometric-series extrapolation. Surprisingly enough, the valence angle BrCN is actually calculated to narrow by 0.27°. As in the case of chlorofulminate,[4] 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 Bromofulminate, Determined Using the CCSD(T) Method and Various cc-pV*nZ* Basis Sets

	cc-pVDZ	cc-pVTZ	cc-pVQZ	Q/5[a]
r(BrC) (Å)	1.8114	1.7971	1.7925	1.7916
r(CN) (Å)	1.1819	1.1672	1.1632	1.1632
r(NO) (Å)	1.2134	1.2099	1.2083	1.2082
ΔE^b (cm^{-1})	561	123	95	100

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

It is worth noting that the equilibrium structural parameters of the BrCNO molecule are determined to be similar to those of the ClCNO molecule,[4] except for the length of the halogen−carbon single bond. For the NCO moiety, the CN and NO bond lengths for both molecules differ by only about 0.001 Å, while the valence angle NCO differs by 1.5°. In comparison to the parent acid, HCNO,[10] substitution of hydrogen by the halogen atom results in lengthening of the CN bond by about 0.01 Å and in narrowing of the valence angle NCO by about 4°. The NO bond length remains nearly the same. The largest difference is observed for the valence angle XCN (X = H, Cl, Br). The HCNO molecule is predicted to be nearly linear at equilibrium,[3,10] while the ClCNO and BrCNO molecules are determined in present calculations to be clearly bent, with the valence angles BrCN and ClCN differing from each other merely by 2.3°.

Table 2 lists the molecular parameters calculated for the linear configuration of the bromofulminate 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 BrCNO chain changes substantially, with the barrier height decreasing by about a factor of 6 on going from the cc-pVDZ to cc-pVQZ basis set. For the cc-pV5Z basis set for all the atoms, the barrier to linearity would be lower by about 2 cm^{-1} than that determined with the cc-pVQZ basis set. Actually, extension of the basis set for the bromine atom alone raises the barrier to linearity by 5 cm^{-1}. The reason for this is not clear.

The BrCN bending potential energy function has been determined by optimizing the structural parameters for various assumed values of the BrCN angle. As for chlorofulminate,[4] the structural parameters were optimized using the cc-pVQZ

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

r(BrC) (Å)	1.7925	1.7945	1.8004	1.8050	1.8103	1.8245
r(CN) (Å)	1.1632	1.1648	1.1696	1.1732	1.1770	1.1864
r(NO) (Å)	1.2083	1.2075	1.2053	1.2037	1.2020	1.1984
∠(BrCN) (deg)	180.	170.	160.	154.80	150.	140.
∠(CNO) (deg)	180.	177.14	174.38	173.04	171.83	169.66
energy (cm^{-1})[a,b]	0.	−27.2	−81.2	−95.0	−79.9	112.8
energy (cm^{-1})[b,c]	0.	−27.7	−84.1	−99.9	−87.6	96.6

[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.

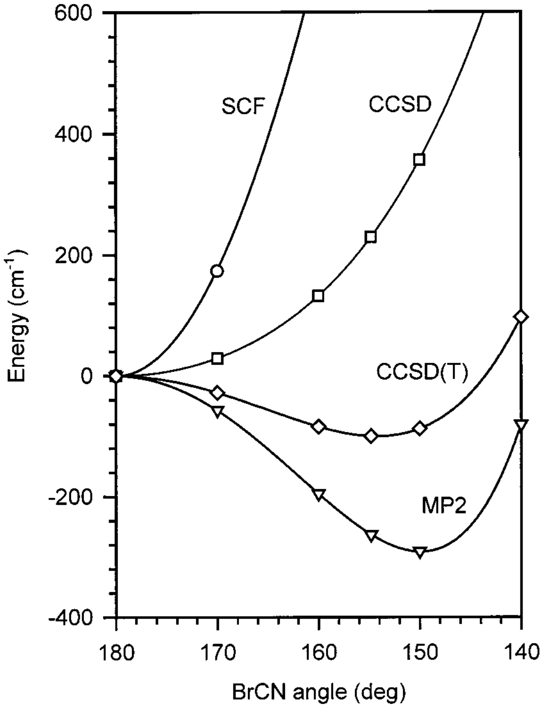

Figure 1. The (relative) total energy of bromofulminate as a function of the BrCN angle, determined using the Q/5 basis set at the SCF, MP2, CCSD, and CCSD(T) levels of theory. The functions are drawn to a common scale.

basis set. Then, the total energy was calculated for each structure using the Q/5 basis set. Results of the calculations are given in Table 3. As was found for the barrier to linearity, the shape of the BrCN bending potential function is determined to be essentially the same for both basis sets. The differences in the calculated total energies amount to at most 16 cm^{-1}. All the structural parameters are found to vary significantly with the BrCN angle, and the calculated changes in the structural parameters resemble closely those determined for chlorofulminate.[4]

The effect of electron correlation on the shape of the BrCN bending potential energy function is illustrated in Figure 1, and the calculated total energies are given in Table 4. The calculations have been performed at various levels of theory, namely self-consistent field (SCF),[16] second-order Møller-Plesset (MP2),[22] and coupled-cluster (CC).[5,6] Within the coupled-cluster method, the effect of connected triple excitations was accounted for by employing the CCSD(T),[12,13] CCSD+T(CCSD),[23] and CCSD−T[24] approaches. The calculations were performed using the one-particle Q/5 basis set and the structural parameters given in Table 3. As for the parent acid[10] and chlorofulminate,[4] the shape of the BrCN bending potential energy function of bromofulminate is due to a balance between different electron correlation effects. At the SCF level, the potential function is predicted to be nearly harmonic (the quartic force constant is smaller by three orders of magnitude than the quadratic one), with a minimum at the linear configuration of the BrCNO chain. Inclusion of the effect of double excitations within the perturbational MP2 approach favors the bent equilibrium configuration, with a minimum at the BrCN angle of about 150° and a barrier to linearity of the BrCNO chain of 291 cm^{-1}. Inclusion of the effects of connected single and double excitations through the CCSD framework results again in the nearly harmonic potential function. However, it is significantly softened in comparison to that determined at the SCF level, with the quadratic force constant being smaller by about a factor of 6. Upon inclusion of the effect of connected triple excitations, the potential function is predicted to be again strongly anharmonic, with a low barrier to linearity of the BrCNO chain. The changes in the shape of the BrCN bending potential energy function upon inclusion of different correlation effects resemble closely those found previously for the HCNO[10] and ClCNO[4] molecules. For all these molecules, the valence correlation energy falls more steeply with the decreasing XCN angle than the Hartree−Fock (HF) total energy raises, thus resulting in the strongly anharmonic XCN bending potential energy function with a minimum at the bent configuration of the XCNO chain. In the case of the parent acid,[10] both effects cancel each other almost completely, leading to the barrier to linearity of the HCNO chain of only a few cm^{-1}. For both halofulminates in question, a change in the correlation energy predominates slightly over that in the HF total energy. Therefore, the barrier to linearity of the BrCNO/ClCNO chain is predicted to be larger by two orders of magnitude than that for the parent acid, nevertheless, yet smaller than the energy of thermal motion at room temperature.

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

∠(BrCN)	180	170	160	154.80	150	140
SCF	0.	173.8	686.5	1070.6	1482.6	2499.2
MP2	0.	−56.6	−194.9	−263.4	−290.8	−81.0
CCSD	0.	28.8	132.3	229.8	356.4	786.4
CCSD(T)	0.	−27.7	−84.1	−99.9	−87.6	96.6
CCSD+T(CCSD)	0.	−38.0	−119.8	−150.6	−151.0	7.9
CCSD−T	0.	−26.1	−79.9	−94.8	−82.5	97.4

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

Table 5 lists the calculated first-order corrections to the total energy of bromofulminate due to the relativistic effects. The corrections were determined for various assumed values of the BrCN angle, with the structural parameters given in Table 3. Inclusion of the relativistic effects, although oversimplified here bearing in mind the form of the cc-pV*n*Z basis set, favors the bent configuration of the molecule. It results thus in a higher barrier to linearity of the BrCNO chain.

To characterize further the BrCN bending potential energy function, the calculated total energies were fitted with an analytical function. As for chlorofulminate,[4] a quadratic potential

TABLE 5: Relativistic Corrections to the Total Energy[a] of Bromofulminate (cm^{-1}) as a Function of the BrCN Angle, Determined at the SCF and CASSCF Levels of Theory Using the Q/5 Basis Set[b]

∠(BrCN)	180	170	160	154.80	150	140
SCF	0.	−2.0	−8.3	−13.4	−19.5	−36.8
CASSCF	0.	−2.9	−11.2	−17.6	−24.5	−41.6

[a] Relative to the correction for the linear configuration, which is determined to be −31.276925 and −31.277397 hartrees at the SCF and CASSCF levels, respectively. Calculated with the structural parameters given in Table 3. [b] See footnote 18.

with a Lorentzian hump was chosen here,

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

The function is expressed in terms of the coordinate ρ, defined as the supplement of the BrCN angle. It involves three parameters: ρ_e, the equilibrium angle; H, the height of a barrier to linearity of the BrCNO chain; and f, the harmonic force constant at $\rho = \rho_e$. The parameters were adjusted in a least-squares fit of this function to the total energies calculated with the Q/5 basis set (Table 3) and corrected for the relativistic effects (CASSCF of Table 5). The root-mean-square deviation of the fit is about 0.06 cm^{-1}, and the parameters are determined to be $H = 119.2$ cm^{-1}, $\rho_e = 26.91°$, and $f = 0.0858$ mdyn Å. The calculated height of the barrier to linearity of the BrCNO chain is smaller than that of the ClCNO chain[4] by only 37 cm^{-1}.

The BrCN bending potential energy function thus determined has been used to calculate the rotation-bending energy levels of bromofulminate. The quantities appearing in the semirigid-bender Hamiltonian[21] are assumed to be functions of the coordinate of the large-amplitude BrCN bending motion ρ. Therefore, the calculated structural parameters of the BrCNO molecule were expanded as polynomials in ρ. From the results quoted above, the expansions were determined to be

$$\begin{aligned} r(\mathrm{BrC}) &= 1.7916 + 0.06392\rho^2 + 0.00343\rho^4 \\ r(\mathrm{CN}) &= 1.1632 + 0.05420\rho^2 - 0.01352\rho^4 \\ r(\mathrm{NO}) &= 1.2082 - 0.02619\rho^2 + 0.01205\rho^4 \\ \gamma &= 16.531\rho - 3.514\rho^3 \end{aligned} \qquad (2)$$

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 BrCN bending (n) quantum numbers. The definitions of these quantum numbers are given in the previous paper.[4] The quantum numbers n and k can be related to the vibrational quantum numbers v_5 and l_5 for the doubly degenerate mode ν_5 in a linear molecule.[25] These relations are: $v_5 = 2n + |k|$ and $l_5 = k$.

TABLE 6: $J = |l_5|$ Rotation-Bending Energy Levels (cm^{-1}) and Changes in the Effective Rotational Constant B (MHz) Due to Excitation of the BrCN Bending Mode, ν_5, of Bromofulminate (the ^{79}Br isotopomer)

$v_5^{l_5}$	energy[a]	ΔB (calcd)[b]	ΔB (expt)[b,c]
0^0	0.0	0.0	0.0
1^1	18.2	4.8	3.9877
1^1	18.2	10.1	9.5073
2^2	54.6	15.3	14.3356
2^0	102.1	−2.7	−3.4395
3^3	103.8	22.9	21.8343
3^1	149.1	8.1	7.4510
3^1	149.1	13.7	13.5542
4^4	162.9	30.3	29.1128
4^2	206.0	20.9	20.5869
4^0	227.5	12.7	11.4022
5^5	230.3	37.3	36.1684
5^3	271.1	29.5	29.2441
5^1	298.5	18.4	17.7283
5^1	298.5	25.3	25.1776
6^6	304.8	44.1	43.0236
6^4	343.2	37.3	37.1411
6^2	372.6	30.5	30.5578
6^0	384.5	26.9	26.4266

[a] The ground-state energy level is calculated to lie 51.7 cm^{-1} above the minimum of the potential energy function. [b] Calculated and experimental ground-state effective rotational constants B are 1733.7 and 1739.9301 MHz, respectively. [c] From analysis of the micro- and millimeter wave spectra, refs 1, 2.

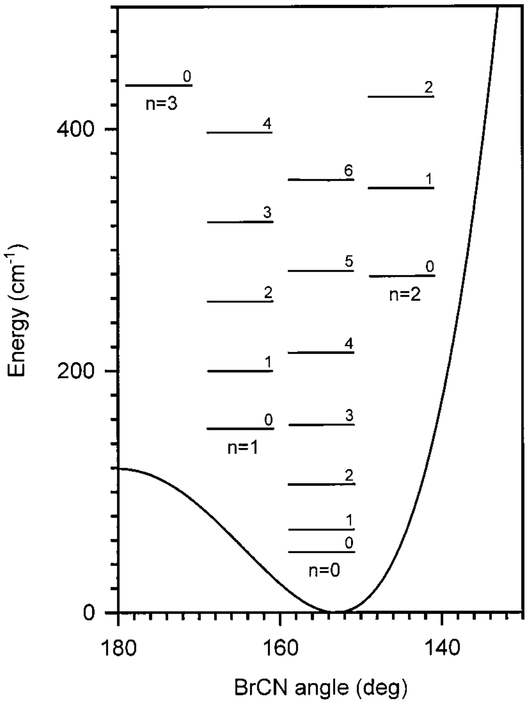

Figure 2. The calculated BrCN bending potential energy function and location of the lowest $J = |k|$ rotation-bending energy levels of bromofulminate (the ^{79}Br isotopomer). Various stacks of the energy levels are shown schematically, each labeled by the BrCN bending quantum number n. Within each stack, the energy levels are labeled by the rotational quantum number k.

The calculated $J = |k|$ rotation-bending energy levels of the main isotopic species of bromofulminate, ^{79}BrCNO, are listed in Table 6. For the sake of comparison with the experimental data,[1,2] the energy levels are labeled with the quantum numbers v_5 and l_5. The location of the energy levels relative to the BrCN bending potential energy function is shown in Figure 2. The energy levels labeled with the same BrCN bending quantum number n are shown as separate stacks, each stack beginning with the rotationless ($J = 0$) level. Comparison with the analogous diagram for chlorofulminate (see Figure 2 of ref 4) shows that location of the energy levels for both molecules is very similar. The ground vibrational state, $n = 0$, is calculated to lie 68 cm^{-1} below the top of a barrier to linearity of the BrCNO chain, while the first excited BrCN 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 BrCN bending motion are determined to lie at the valence angle BrCN of 145° and 164°. Although transitions between the BrCN bending energy levels have not been observed experimentally so far, the relative

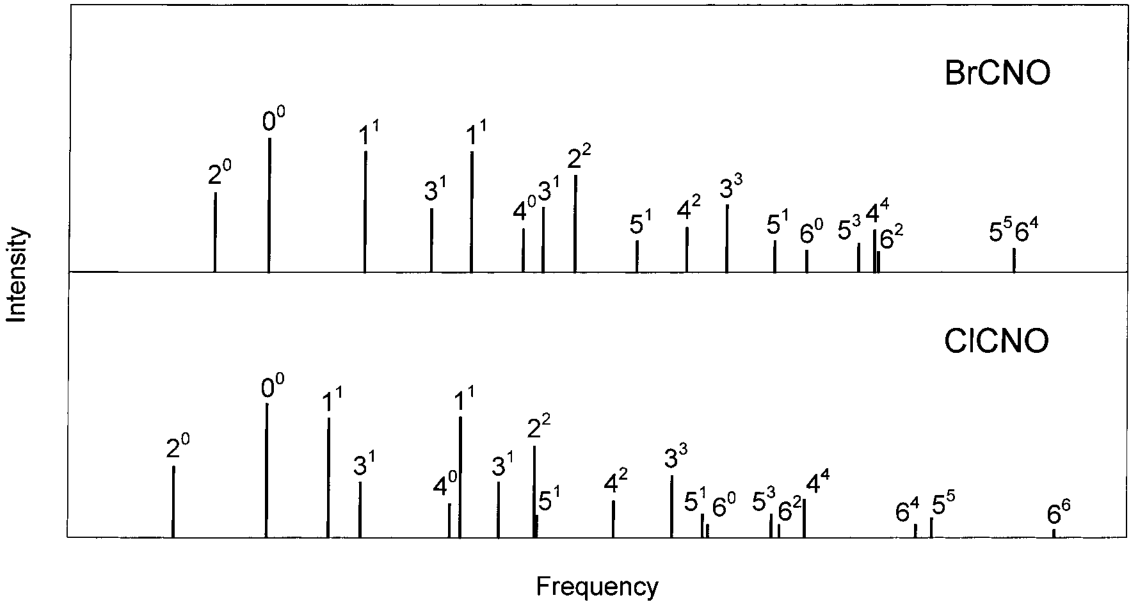

Figure 3. The calculated patterns of vibrational satellites of the *a*-type $J + 1 \leftarrow J$ rotational transition for bromo- and chlorofulminate (the ^{79}Br and ^{35}Cl isotopomers, respectively). The lines are labeled by the vibrational quantum numbers $v_5^{l_5}$. The frequency axis for bromofulminate is stretched, in comparison to that for chlorofulminate, by a factor of 1.5 (the ratio of the ground-state effective rotational constants B for the ClCNO and BrCNO molecules). The effect of intensity doubling for unresolved pairs of lines is not taken into account.

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 bromofulminate. The $1^1 - 0^0$ energy level separation is estimated in this way[2] to be 21 ± 5 cm^{-1}. The predicted ab initio value of 18.2 cm^{-1} falls well within the experimental error bars.

Similar location of the rotation-bending energy levels for bromo- and chlorofulminate seems to be rather surprising at first sight in view of the large difference in masses of the bromine and chlorine atoms and of a close resemblance of the BrCN and ClCN bending potential energy functions. Examination of the $\mu_{\rho\rho}$ term, which governs the kinetic energy of the BrCN/ClCN bending motion (see eqs 1−5 of ref 21), reveals, however, that the contribution related to the halogen atomic mass is smaller by at least one order of magnitude than those related to masses of the other atoms. Therefore, the $\mu_{\rho\rho}$ terms are calculated to be nearly the same for both the BrCNO and ClCNO molecules, with the ratio being approximately 0.8.

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.[25] The effective rotational constant B for the ground vibrational state of the main isotopic species of bromofulminate is determined in this way to be 1733.7 MHz. The predicted value is in excellent agreement with the experimental value of 1739.9301 MHz.[1] The rotational constant B changes substantially and, for many energy levels, irregularly with excitation of the BrCN bending mode. The predicted and observed changes are listed in Table 6. As can be seen, the ab initio and experimental values agree to about 1 MHz for 18 excited energy levels ranging up to nearly 400 cm^{-1} above the ground state.

Figure 3 illustrates the calculated patterns of vibrational satellites in the rotational spectra of the BrCNO and ClCNO molecules. Part of the spectrum for the *a*-type $J + 1 \leftarrow J$ rotational transition is shown. The approximate relative intensities of lines, at room temperature, were determined using the expressions for line strengths of a linear molecule.[25] As can be seen, the patterns are predicted to be similar for both molecules. Comparison of the calculated pattern with that observed for the ^{79}Br and ^{81}Br isotopomers of bromofulminate (see Figure 1 of ref 1) shows that agreement with the experimental data can be called nothing but excellent, especially because the observed pattern is highly anomalous. Such agreement validates the calculated structure and BrCN bending potential energy function of bromofulminate by any standard.

It is worth noting that similar changes in the effective rotational constant B with excitation of skeletal bending mode have already been observed for methyl isothiocyanate, CH_3-NCS.[26,27] The CH_3NCS molecule is the example of a quasi-symmetric top with a medium barrier to linearity of the heavy-atom skeleton. In contrast to the molecules considered here, it undergoes two large-amplitude motions, namely the CNC bending motion and internal rotation of the methyl group. The shape of the CNC bending potential function, location of the energy levels of large-amplitude motions, and the pattern of vibrational satellites in the rotational spectrum of methyl isothiocyanate resemble closely those discussed here for bromo- and chlorofulminate.

To quantify quasilinearity of the BrCNO chain, the parameter γ_0 can be calculated, ranging from -1 for an ideal linear molecule to $+1$ for an ideal bent molecule.[28] From the calculated rotation-bending energy levels of bromofulminate, the parameter γ_0 is determined to be 0.29. For the HCNO and ClCNO molecules, the parameter γ_0 is determined to be -0.66 [3] and 0.35,[4] respectively. This, as well as comparison of the calculated patterns of vibrational satellites (Figure 3), indicates that the BrCNO molecule is closer to the linear-molecule limit than the ClCNO molecule.

In conclusion, the BrCNO molecule is shown clearly to be an another prominent example of a quasilinear molecule, along with the parent acid, HCNO,[3] and chlorofulminate, ClCNO.[4] The results reported previously[4] and in this paper demonstrate that the CCSD(T) method in conjuction with the large one-particle basis set of *spdfgh* quality provides a remarkably accurate description of the electronic structure of halofulminates.

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