

Vibrational frequencies and structural determination of thiocyanogen

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Abstract

The vibrational frequencies and corresponding normal mode assignments of thiocyanogen are examined theoretically using the Gaussian03 set of quantum chemistry codes. All normal modes were successfully assigned to one of six types of motion (C≡N stretch, C–S stretch, S–S stretch, S–C≡N bend, C–S–S bend, C–S–S–C torsion) utilizing the C_2 symmetry of the molecule. Molecular orbitals and bonding are examined.

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1. Introduction

The synthesis and isolation of thiocyanogen (SCN)₂ was first reported in 1919 [1]. However, its presence in aqueous solution was postulated in an earlier experiment [2] where the standard electrode potential for the conversion of thiocyanogen to the thiocyanate ion was measured and reported. Several methods for preparing thiocyanogen have appeared [1,3–9], and it has proven to be an extremely useful reagent in the synthesis of novel organic and inorganic compounds [10–15]. The structure and bonding of thiocyanogen has been examined in theoretical studies [16,17].

Due to its unusual bonding and symmetry, thiocyanogen is an excellent candidate for a quantum chemical normal mode analysis. Experimental infrared and Raman spectra of thiocyanogen exist in the literature [18–28]. However, a quantum chemical analysis of the vibrational modes of thiocyanogen has not been performed to date. A detailed quantum chemical study will aid in making definitive assignments to the fundamental normal modes of thiocyanogen and in clarifying the experimental data available for this important molecule. In this study the infrared and Raman spectra of thiocyanogen are examined using

the Gaussian03 suite of quantum chemical codes [29] and compared against available experimental data.

2. Computational methods

The vibrational frequencies of thiocyanogen were calculated at the Hartree–Fock, DFT (B3LYP), and MP2 levels of theory using the standard 6-311G* basis set. The calculations utilized the C_2 symmetry [30] of the thiocyanogen molecule (see Fig. 1). Thiocyanogen has a skew-structure, similar to hydrogen peroxide [31]. The cyanide groups are rotated approximately 90 degrees relative to each other along the S–S axis. The computations were performed using the Gaussian03 program package [29]. Each of the vibrational modes was assigned to one of six types of motion (C≡N stretch, C–S stretch, S–S stretch, S–C≡N bend, C–S–S bend, C–S–S–C torsion) by means of visual inspection using the Gaussview program [32].

There is always some choice in defining internal coordinates. However, the coordinates described above form a complete set and match quite well the motions observed using the Gaussview program. Combining the results of the Gaussview program [33] with the symmetry considerations, vibrational frequency assignments were made with a high degree of confidence.

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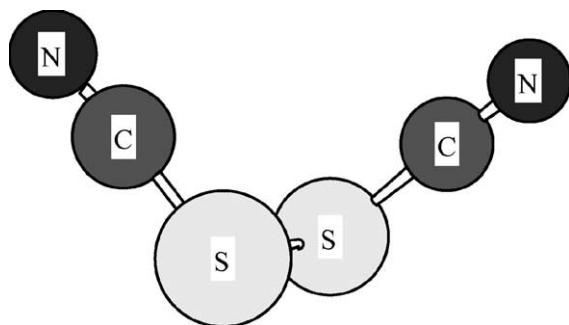


Fig. 1. Structure of thiocyanogen.

3. Results

Tables 1–3 present the calculated vibrational frequencies for thiocyanogen calculated at the Hartree–Fock, DFT (B3LYP), and MP2 levels of theory. Correction factors for the different types of vibrational modes were calculated following a procedure that was previously proposed [33]. The correction factors are obtained by taking the average of the ratios between the computed and experimental frequencies for all modes of a given motion type. There is very little variation in the ratios for all modes within a given motion type. This indicates that the procedure should lead to reliable predictions. The computed correction factors calculated at the Hartree–Fock, DFT (B3LYP), and MP2 levels of theory are presented in Table 4. These correction

Table 1
Normal modes of thiocyanogen calculated at the Hartree–Fock level of theory using the standard 6-311G* basis set

Symmetry	Normal mode	Calculated frequency	IR intensity ^a	Raman activity ^b	Assignment	Experimental frequency ^c	Corrected frequency ^d
A	ν_1	2541	4	168	C≡N stretch	2159	2158
	ν_2	725	8	3	S–C stretch	668	669
	ν_3	552	2	41	S–S stretch	489	489
	ν_4	453	4	5	S–C≡N bend	399	393
	ν_5	437	0	7	S–C≡N bend	368	379
	ν_6	157	0	7	C–S–S bend	163	146
	ν_7	59	4	7	C–S–S–C torsion	–	53
B	ν_8	2543	7	90	C≡N stretch	2158	2159
	ν_9	728	9	1	S–C stretch	673	672
	ν_{10}	496	1	1	S–C≡N bend	432	430
	ν_{11}	422	6	1	S–C≡N bend	368	366
	ν_{12}	175	12	6	C–S–S bend	163	163

^a Units of IR intensity are km/mol.

^b Units of Raman scattering activity are Å⁴/amu.

^c [21,23,25].

^d Raw calculated frequencies multiplied by the correction factors in Table 4.

Table 2
Normal modes of thiocyanogen calculated at the DFT (B3LYP) level of theory using the standard 6-311G* basis set

Symmetry	Normal mode	Calculated frequency	IR intensity ^a	Raman activity ^b	Assignment	Experimental frequency ^c	Corrected frequency ^d
A	ν_1	2260	1	256	C≡N stretch	2159	2156
	ν_2	674	3	5	S–C stretch	668	667
	ν_3	461	1	25	S–S stretch	489	489
	ν_4	411	2	2	S–C≡N bend	399	403
	ν_5	369	0	21	S–C≡N bend	368	362
	ν_6	137	0	9	C–S–S bend	163	147
	ν_7	54	3	9	C–S–S–C torsion	–	54
B	ν_8	2265	1	122	C≡N stretch	2158	2161
	ν_9	681	2	1	S–C stretch	673	674
	ν_{10}	437	1	0	S–C≡N bend	432	429
	ν_{11}	381	2	0	S–C≡N bend	368	374
	ν_{12}	152	8	7	C–S–S bend	163	163

^a Units of IR intensity are km/mol.

^b Units of Raman scattering activity are Å⁴/amu.

^c [21,23,25].

^d Raw calculated frequencies multiplied by the correction factors in Table 4.

Table 3
Normal modes of thiocyanogen calculated at the MP2 level of theory using the standard 6-311G* basis set

Symmetry	Normal mode	Calculated frequency	IR intensity ^a	Raman activity ^b	Assignment	Experimental frequency ^c	Corrected frequency ^d
A	ν_1	2122	1	111	C≡N stretch	2159	2156
	ν_2	699	2	3	S–C stretch	668	669
	ν_3	486	1	25	S–S stretch	489	489
	ν_4	389	1	4	S–C≡N bend	399	397
	ν_5	372	0	2	S–C≡N bend	368	380
	ν_6	137	0	6	C–S–S bend	163	145
	ν_7	53	3	7	C–S–S–C torsion	–	53
B	ν_8	2127	1	63	C≡N stretch	2158	2161
	ν_9	703	2	1	S–C stretch	673	672
	ν_{10}	434	1	0	S–C≡N bend	432	443
	ν_{11}	343	2	0	S–C≡N bend	368	350
	ν_{12}	154	9	6	C–S–S bend	163	163

^a Units of IR intensity are km/mol.

^b Units of Raman scattering activity are Å⁴/amu.

^c [21,23,25].

^d Raw calculated frequencies multiplied by the correction factors in Table 4.

factors were used to generate the corrected (predicted) frequencies in the last column of Tables 1–3, respectively.

Fig. 2 presents a view of the normal modes of using the NCAPlot utility in SPIROVIB [34]. The corrected DFT frequencies are also presented. Table 5 presents the selected geometric parameters for thiocyanogen. Thiocyanogen has a skew-structure with the cyanide groups rotated approximately 90 degrees relative to each other along the S–S axis.

Fig. 3 presents the valence occupied molecular orbitals [35] of thiocyanogen. The atomic core orbitals are not shown. Orbitals 15–20 are linear combinations of the 2s orbitals from the carbon and nitrogen atoms along with the 3s orbitals from the sulfur atoms. Orbitals 21–29 are linear combinations of p-orbitals (2p orbitals from carbon and nitrogen atoms and 3p orbitals from the sulfur atoms).

It is difficult to determine the bonding of thiocyanogen from Fig. 3. However, the Mulliken overlap terms are very close to what would be expected. The overlap term between the nitrogen and carbon atoms is very large ($Q_{CN}=0.935$), consistent with a formal triple bond. The overlap terms for the other two bonds are considerably smaller ($Q_{CS}=0.135$ and $Q_{SS}=0.106$). Typical values for Mulliken overlap terms for single bonds are approximately 0.2–0.3. The Mulliken overlap terms suggest that the S–C and S–S bonds in thiocyanogen are relatively weak single bond. The Mulliken charge distribution is presented in Table 6.

Table 4
Correction factors for thiocyanogen

	Hartree–Fock	DFT (B3LYP)	MP2
C≡N stretch	0.8491	0.9540	1.0160
S–C stretch	0.9229	0.9897	0.9565
S–S stretch	0.8859	1.0607	1.0062
S–C≡N bend	0.8665	0.9806	1.0208
C–S–S bend	0.9314	1.0724	1.0584
C–S–S–C torsion	0.90	1.00	1.00

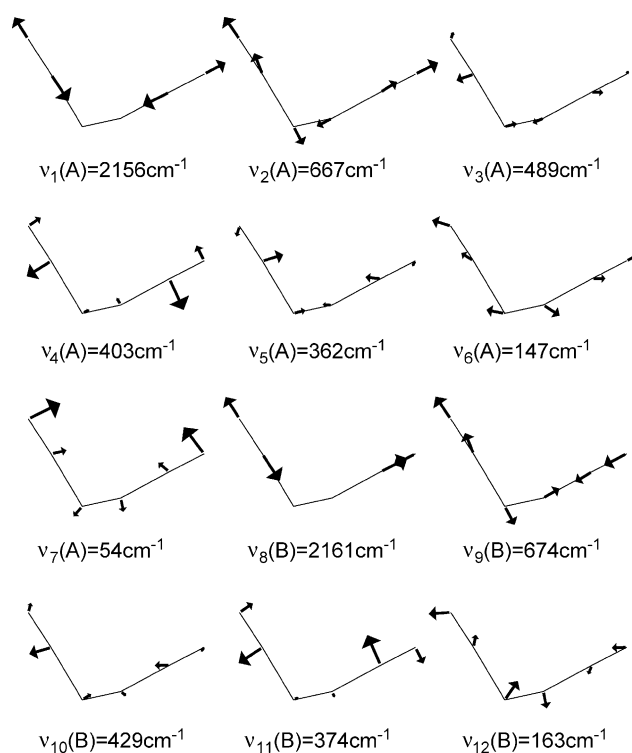


Fig. 2. Normal modes of thiocyanogen.

Table 5
Geometric parameters for thiocyanogen

	Hartree–Fock	DFT (B3LYP)	MP2
C≡N	113.0	115.8	118.0
C–S	170.6	169.9	169.6
S–S	208.3	214.2	209.9
N≡C–S	176.8	176.0	176.4
C–S–S	101.0	101.3	99.6
C–S–S–C	87.9	89.4	85.6
C≡N–S–S	–177.2	–177.3	–176.6

Distances are presented in pm and angles in degrees.

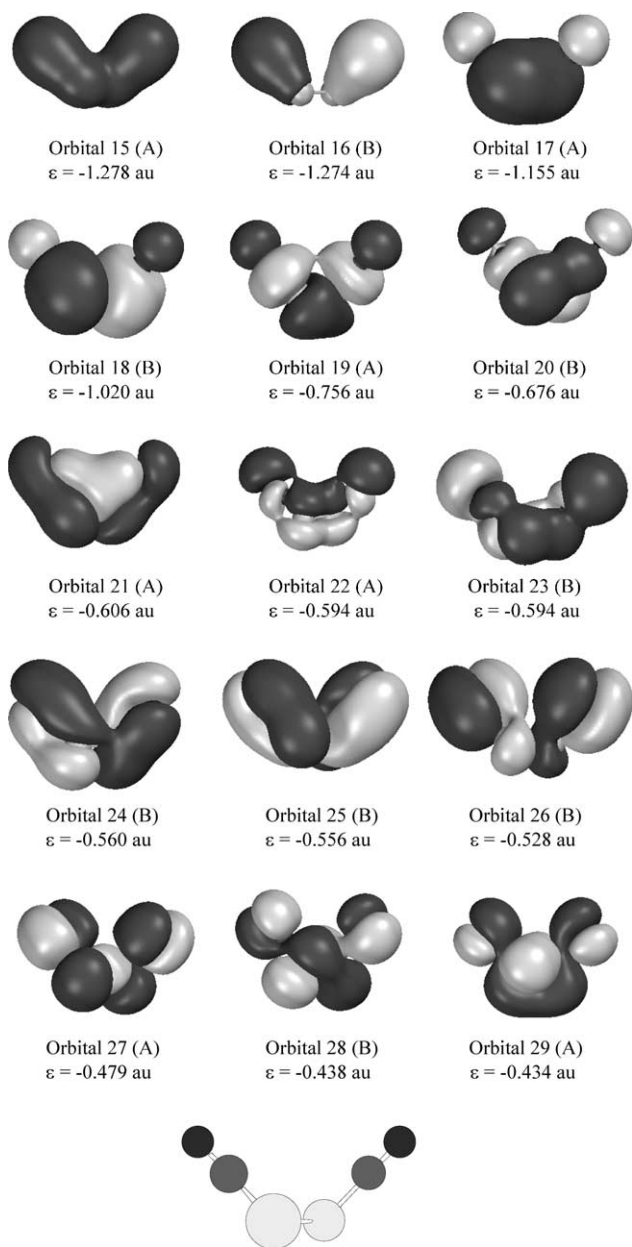


Fig. 3. Valence molecular orbitals of thiocyanogen.

4. Summary and conclusions

A normal mode analysis of thiocyanogen was completed with good results. Normal modes were calculated at the Hartree–Fock, DFT (B3LYP) and MP2 levels of theory using the standard 6-311G* basis. Computed vibrational modes were compared against available experimental information

Table 6
Mulliken charge distribution for thiocyanogen

	Hartree–Fock	DFT (B3LYP)	MP2
S	0.248	0.234	0.216
C	0.036	−0.036	0.035
N	−0.284	−0.198	−0.251

that exists in the literature. All normal modes were successfully assigned to one of six types of motion ($C\equiv N$ stretch, C–S stretch, S–S stretch, S–C $\equiv N$ bend, C–S–S bend, C–S–S–C torsion) predicted by a group theoretical analysis. Infrared and Raman intensities calculated and reported.

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