



Experimental and theoretical vibrational study of methylene bis(thiocyanate), $\text{CH}_2(\text{SCN})_2$. A comparison with thiocyanogen, $(\text{SCN})_2$

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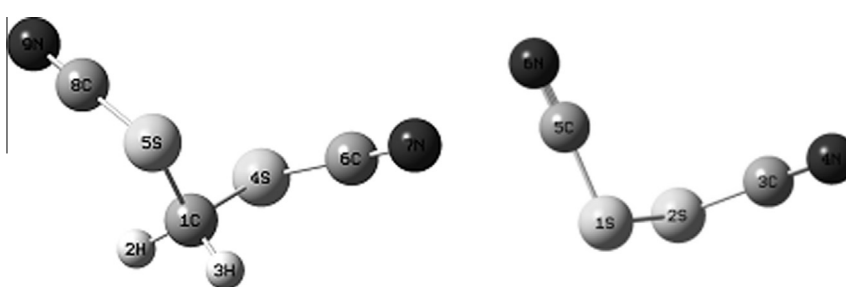
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HIGHLIGHTS

- The infrared and Raman spectra of $\text{CH}_2(\text{SCN})_2$ are obtained.
- Bands in the spectra of the $\text{CH}_2(\text{SCN})_2$ and $(\text{SCN})_2$ molecules are assigned after comparison with the calculated frequencies.
- The experimental frequencies of both molecules are reproduced with calculated Scaled Quantum Mechanics force fields.
- A comparison of the internal force constants shows similar values for the equivalent bonds in both molecules.

GRAPHICAL ABSTRACT



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ABSTRACT

The infrared and Raman spectra of methylene bis(thiocyanate), $\text{CH}_2(\text{SCN})_2$, were obtained. The observed bands were assigned to the different normal modes of vibration using the results of a DFT calculation of the molecular vibrational properties. These results and the experimental data were used to define a Scaled Quantum Mechanics force field for the molecule. A similar treatment was applied to the thiocyanogen molecule, $(\text{SCN})_2$, for which the experimental frequencies were already reported in the literature. The sets of internal force constants for both molecules show very similar values.

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Introduction

Methylene bis(thiocyanate) (MBT) is a crystalline solid used as microbicide, fungicide, algicide and disinfectant which found numerous uses in water-cooling systems, pulp and paper mills,

wood and leather processing, oil drilling industry and paint manufacturing, between others [1].

The crystalline structure of MBT is already known [2]. However no information has been found in the literature about its infrared and Raman spectra and their corresponding interpretation. Considering that the knowledge of the vibrational properties of MBT could be useful in view of the numerous practical uses of the substance, their vibrational spectra were obtained and the observed

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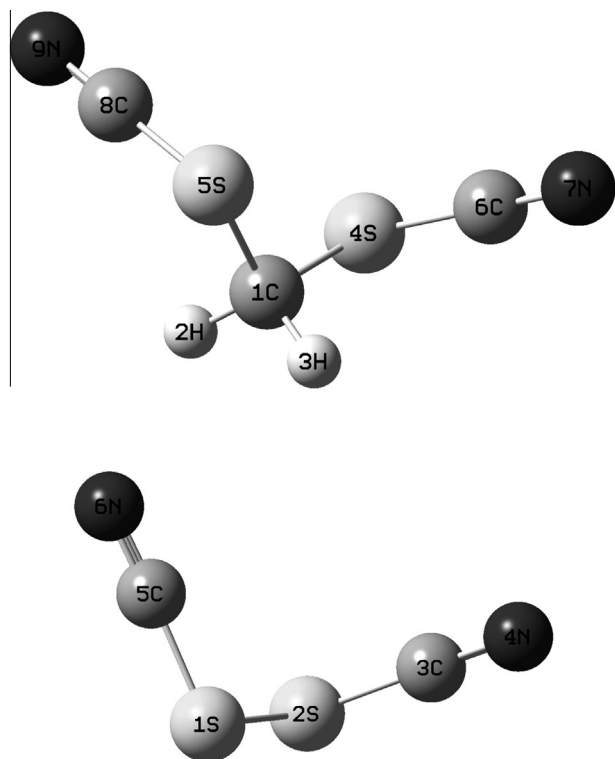


Fig. 1. Molecular structures of MBT [$\text{CH}_2(\text{SCN})_2$] and thiocyanogen [$(\text{SCN})_2$].

bands conveniently assigned with the aid of quantum chemistry calculations. The band assignments were subsequently used for a calculation of the corresponding force constants using the approach of Pulay [3].

The related molecule thiocyanogen, $(\text{SCN})_2$, was also studied in order to compare its force field with that calculated for MBT. The structure of this molecule was studied theoretically using the semi-empirical methods MNDO [4] and SINDO1 [5]. Later, Jensen used Hartree–Fock, DFT (B3LYP), and MP2 levels of theory and the 6-311G^{*} basis set to calculate the structure and vibrational frequencies of thiocyanogen [6]. The experimental frequencies of vibration were also reported [6 and references therein].

Table 1
Optimized geometric parameters for the molecules $\text{CH}_2(\text{SCN})_2$ and $(\text{SCN})_2$ and experimental values for $\text{CH}_2(\text{SCN})_2$.

	$\text{CH}_2(\text{SCN})_2$		$(\text{SCN})_2$ Calc. ^c
	Calc. ^a	Exp. ^b	
Bonds (Å)			
S–CH ₂	1.829	1.808(6)	–
S–CN	1.689	1.677(9)	1.693
C≡N	1.155	1.194(12)	1.155
C–H	1.086	–	–
S–S	–	–	2.098
Angles (°)			
C–S–C	99.6	98.2(4)	–
S–C≡N	178.2	176.4(10)	176.3
S–C–S	117.1	115.0(5)	–
C–S–S	–	–	102.1
H–C–H	109.6	110.5 ^d	–
C–S–C–S	71.0	77.8 ^d	–
N≡C–S–S	–	–	176.6
C–S–S–C	–	–	89.3

^a B3LYP/6-311++G(3df, 3pd) calculations.

^b Ref. [2].

^c B3LYP/6-311+G(3df) calculations.

^d Calculated from the fractional coordinates given in Ref. [2].

Table 2

Observed bands in the infrared and Raman spectra of $\text{CH}_2(\text{SCN})_2$.

IR ^a	Raman ^b
3017 (s)	3018 (8)
2956 (s)	2956 (19)
2166 (vs)	2167 (100)
–	1493 (4) ?
1380 (s)	1381 (11)
1209 (s)	–
1159 (m)	1149 (6)
857 (s)	860 (4)
808 (w)	812 (1)
698 (s)	698 (12)
668 (m)	680 (7)
638 (m)	637 (34)
–	474 (3)
463 (m)	459 (3)
402 (m)	402 (4)
272 (m)	270 (26)
237 br	246 (10)
140 (w)	137 (27)
77 (w)	77 (81)

^a v, very; s, strong; m, medium; w, weak; br, broad.

^b Relative Raman intensities appear in parentheses.

Experimental

MBT was prepared reacting CH_2Br_2 with NaSCN, according with a procedure reported in the literature [7]. The infrared spectrum of the obtained substance was identical with that found in the spectral data base for organic compounds of the National Institute of Advanced Industrial Science and Technology (AIST), Japan.

The infrared spectra of MBT in KBr pellets were measured in the region 4000–400 cm^{-1} using a Perkin–Elmer GX FTIR instrument. The FIR spectra (400–50 cm^{-1}) were run with the substance in polyethylene pellets using a Nicolet Nexus FTIR instrument. The Raman spectra were run on the pure, solid substance by means of a Bruker IFS 66 instrument provided with the FRA 106 accessory, which uses 1064 nm radiation for sample excitation.

Calculations

The optimized molecular geometry, frequencies corresponding to the normal modes of vibration, Cartesian harmonic force constants and infrared and Raman intensities were calculated for both molecules by means of density functional theory (DFT) techniques. All calculations were made for the isolated molecules using the Gaussian 03 set of programs [8] with the B3LYP functional [9,10] and the 6-311++G(3df,3pd) basis set [11,12]. That combination gave the best approximation to the vibrational frequencies, as resulted from a series of exploratory calculations using different methods and basis sets.

The obtained Cartesian force constants were transformed to natural (local symmetry) coordinates as defined by Fogarasi et al. [13] through the corresponding B matrix [14], calculated with a standard program. The resulting force fields were subsequently scaled using the formalism of Pulay et al. [3], according to which the diagonal force constants are multiplied by scale factors f_i , f_j, \dots and the corresponding interaction constants are multiplied by $(f_i f_j)^{1/2}$, adjusting these factors until the best reproduction of the experimental frequencies was obtained. No anharmonicity corrections of these frequencies were made because of the lack of the necessary experimental data.

The resulting SQM (Scaled Quantum Mechanics) force fields were then used to calculate the potential energy distribution (PED) of the studied molecules, which represents the contribution of each main force constant to the different normal modes of

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