

Vibrational spectroscopic studies of acetaldehyde semicarbazone

SOMI SEBASTIAN¹, Y. SHEENA MARY²,
HEMA TRESA VARGHESE² and C.YOHANNAN PANICKER^{3*}

¹Department of Electronics and Communication Engineering,

Sree Budha College of Engineering, Pattoor, Alapuzha - 690 529 (India).

²Department of Physics, Fatima Mata National College, Kollam, Kerala (India).

³Department of Physics, TKM College of Arts and Sciecne, Kollam, Kerala (India).

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ABSTRACT

FT-IR and FT-Raman spectra of acetaldehyde semicarbazone were recorded and analyzed. The vibrational wavenumbers were calculated theoretically using Gaussian03 set of quantum chemistry codes. The first hyperpolarizability, infrared intensities and Raman activities are also reported. The calculated first hyperpolarizability is comparable with the reported values of similar derivatives and is an attractive object for future applications in non-linear optics. The geometrical parameters are in agreement with that of reported similar structures.

Key words: FT-IR, FT-Raman, semicarbazone, hyperpolarizability.

INTRODUCTION

Semicarbazones and thiosemicarbazones have been investigated due to in their coordination behaviour, analytical applications¹, and biological properties such as antibacterial², antimalarial³, antifungal⁴, and antitumor⁵. Semicarbazones represent a very interesting group of ligands to several main group metals d-block elements and f-block elements^{1,6-8}. Semicarbazones of aromatic and unsaturated carbonyl compounds have anticonvulsant properties and their advantage over the analogous thiosemicarbazones is their lower neurotoxicity⁹. Semicarbazones have an inhibitory effect on nitric oxide synthesis, which protects the vascular system¹⁰. Semicarbazone family crystals have non linear optical behavior¹¹⁻¹⁴. Computational method is at present widely used for simulating IR spectrum. Such simulations are indispensable tools to perform normal coordinate analysis so that modern vibrational spectroscopy is unimaginable

without involving them. In the present study, the IR, Raman and theoretical calculations of the wavenumbers of the title compound are reported. Nonlinear optics deals with the interaction of applied electromagnetic fields in various materials to generate new electromagnetic fields, altered in wavenumber, phase, or other physical properties¹⁵. Organic molecules are able to manipulate photonic signals efficiently. They are of importance in technologies such as optical communication, optical computing, and dynamic image processing^{16,17}. The hyperpolarizability of the title compound is also calculated in the present study.

EXPERIMENTAL

The FT-IR spectrum was recorded on a DR/Jasco FT-IR-6300 spectrometer in KBr pellets. The spectral resolution was 4 cm⁻¹. The FT-Raman spectrum was obtained on a Bruker RFS 100/S, Germany. For excitation of the spectrum the

emission of Nd:YAG laser was used, excitation wavelength 1064 nm, maximal power 150 mW, measurement on solid sample. The spectral resolution after apodization was 4 cm⁻¹.

Computational details

The vibrational wavenumbers were calculated using the Gaussian03 software package on a personal computer¹⁸. The computations were performed at HF/6-31G(d) (6D, 7F) and B3LYP/6-31G(d) (6D, 7F) levels of theory to get the optimized geometry and vibrational wavenumbers of the normal modes of the title compound. DFT calculations were carried out with Becke's three-parameter hybrid model using the Lee-Yang-Parr correlation functional (B3LYP) method. The wavenumber values computed contain known systematic errors¹⁹ and we therefore, have used the scaling factor values of 0.8929 and 0.9613 for HF and DFT basis sets. The absence of imaginary values of wavenumbers in the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy.

RESULTS AND DISCUSSION

The observed IR and Raman bands and calculated (scaled) wavenumbers and assignments are given in Table 1. In the spectra of methyl esters the overlap of the region in which both asymmetric stretching²⁰ $\nu_{as}CH_3$ absorb with a weak to medium intensity (2985 ± 25 and 2970 ± 30 cm⁻¹) is not large and regularly seen above 3000 cm⁻¹. The computed wavenumbers of modes corresponding to $\nu_{as}CH_3$ groups are 3023, 2966 cm⁻¹. For the title compound, band at 2971 cm⁻¹ in the IR spectrum and 3000 cm⁻¹ in the Raman spectrum is assigned as asymmetrical methyl stretching modes. The symmetrical stretching mode ν_sCH_3 is expected in the range 2920 ± 80 cm⁻¹ in which all the three C-H bonds extend and contract in phase²⁰. The bands seen at 2920 (DFT), 2914 (IR) cm⁻¹ and 2910 cm⁻¹ (Raman) are assigned as these modes. Two bending vibrations can occur within a methyl group. With methyl esters the overlap of the regions in which methyl asymmetric deformations are active (1460 ± 25 and 1450 ± 15 cm⁻¹) is quite strong, which leads to many coinciding wavenumbers²⁰. This is obvious, not only for the asymmetric deformations, but also for the symmetric deformations²⁰ mostly

displayed in the range 1380 ± 15 cm⁻¹. The B3LYP calculations give 1449, 1448 and 1385 cm⁻¹ as asymmetric and symmetric CH₃ deformations for the title compound. Experimentally $\delta_{as}CH_3$ vibration is observed in the Raman spectrum at 1452, 1435 cm⁻¹ and at 1448 cm⁻¹ in the IR spectrum while δ_sCH_3 vibrations are observed at 1379 cm⁻¹ in the IR spectrum, 1376 cm⁻¹ in the Raman spectrum. The methyl rocking wavenumbers are expected in the regions²⁰ 1100 ± 95 and 1080 ± 80 cm⁻¹. The bands calculated at 1117, 953 cm⁻¹ are assigned as rocking modes of the methyl groups. The rocking mode is observed at 965 cm⁻¹ in the IR spectrum. The NH₂ asymmetric stretching vibrations²⁰ give rise to a strong band in the region 3390 ± 60 cm⁻¹ and the symmetric NH₂ stretching in the region 3210 ± 60 cm⁻¹ with a somewhat weaker intensity. The DFT calculations give these modes at 3526 and 3479 cm⁻¹ as $\nu_{as}NH_2$ and ν_sNH_2 respectively. Baran *et al.*²¹ reported $\nu_{as}NH_2$ at 3381, 3186 and 3398, 3203 cm⁻¹ respectively for copper complexes of L-asparagine and L-glutamine. The NH₂ deformation band²⁰ δNH_2 is expected in the region 1610 ± 30 cm⁻¹. For the title compound, the δNH_2 band is observed at 1594 cm⁻¹ in IR, 1590 cm⁻¹ in Raman and at 1595 cm⁻¹ theoretically. δNH_2 is reported at 1680 (IR), 1694 (Raman) and 1664 (IR), 1695 cm⁻¹ (Raman) for metal complexes of L-asparagine and L-glutamine²¹. The in-plane NH₂ rock absorbs weakly to moderately in the region²⁰ 1125 ± 45 cm⁻¹. For L-glutamic acid 5-amide, ρNH_2 is reported to be at 1136 (IR), 1133 (Raman) and 1134 cm⁻¹ theoretically²². The band at 1065 cm⁻¹ in Raman, 1059 cm⁻¹ in IR and 1059 cm⁻¹ (DFT) are assigned to ρNH_2 for the title compound. The amide band, absorbing in the region 775 ± 45 cm⁻¹, is assigned to NH₂ out-of-plane twist and wagging mode ρNH_2 is expected in the region²⁰ 670 ± 60 cm⁻¹. The NH₂ wag is usually clearly separated from the twist and is easy to recognize by its broad band structure. The out-of-plane twist τNH_2 is observed at 865 cm⁻¹ theoretically. The wagging mode ωNH_2 is observed at 730 cm⁻¹ (DFT) for the title compound. The wagging mode ρNH_2 is reported to be at 669, 675 (IR) and 663, 645 cm⁻¹ (Raman)^{22, 23}. The carbonyl stretching C=O vibration²⁰ is expected in the region 1715-1680 cm⁻¹ and in the present study this mode appears at 1716 cm⁻¹ in the IR spectrum. The DFT calculations give this mode at 1741 cm⁻¹. The γ C=O in-plane deformation and the out-of-

Table 1: Calculated vibrational wavenumbers (scaled), measured infrared and Raman band positions and assignments

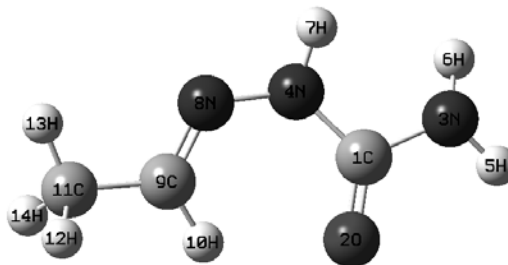
6-31G(d) (6D,7F)			M6-31G(d) (6D,7F)			$\nu_{(IR)}$	$\nu_{(Raman)}$	Assignments
ν cm ⁻¹	IR Intensity (KM/Mole)	Raman activity (A**4/AMU)	ν cm ⁻¹	IR Intensity (KM/Mole)	Raman activity (A**4/AMU)	cm ⁻¹	cm ⁻¹	
3507	47.12	54.47	3526	27.46	74.67			$\nu_{as}NH_2$
3446	33.79	70.72	3479	22.57	89.75			ν_sNH_2
3405	51.33	85.00	3419	27.90	131.20	3426, 3314	3438	νNH
3006	12.86	37.02	3075	2.47	27.31	3074		νCH
2957	12.09	73.64	3023	11.97	74.95		3000	$\nu_{as}CH_3$
2908	26.02	100.23	2966	20.51	114.67	2971		$\nu_{as}CH_3$
2862	25.56	156.83	2920	25.70	211.10	2914	2910	ν_sCH_3
1771	342.34	1.48	1741	204.36	5.76	1716		νCO
1738	16.07	32.73	1659	0.60	66.44	1662	1672	$\nu C=N$
1613	120.46	4.16	1595	83.94	4.79	1594	1590	δNH_2
1521	211.71	3.38	1493	197.48	7.74		1500	δNH
1450	7.57	22.15	1449	10.82	26.05		1452	$\delta_{as}CH_3$
1447	12.39	23.09	1448	23.88	38.84	1448	1435	$\delta_{as}CH_3$
1403	48.12	4.85	1385	38.99	15.74	1379	1376	δ_sCH_3
1358	78.38	12.50	1335	80.10	17.73	1320	1328	$\delta CH, \nu CN$
1302	233.40	0.75	1284	212.48	0.86			$\delta NH, \nu CN$
1136	28.19	1.54	1120	51.14	5.52	1123	1130	νNN
1121	37.87	3.84	1117	48.94	5.77			ρCH_3
1086	0.95	1.65	1059	9.36	12.62	1059	1065	ρNH_2
1076	6.06	3.75	1048	0.64	0.29			ρNH
973	13.25	3.27	953	3.78	4.14	965		ρCH_3
906	7.50	5.77	883	12.46	5.83	886	887	νCC
865	26.70	7.68	865	16.27	5.17			τNH_2
767	101.35	0.32	731	51.37	1.20	738		$\delta C=O,$
749	41.70	1.98	730	16.54	3.17			$\omega NH, \omega NH_2$
597	64.07	2.59	557	219.96	5.97			δCC
537	12.82	3.11	528	112.77	2.37			$\gamma C=O$
522	312.90	3.04	520	72.40	2.14	500		$\delta C=N$
391	39.41	3.08	385	10.35	4.09		375	γCNH
385	36.85	2.60	361	50.37	2.93			δCC
337	9.86	0.98	324	13.60	0.61		328	$\delta C=N$
316	5.10	0.31	314	2.92	0.68			$\gamma C=NN$
204	11.32	1.39	201	2.62	0.90		210	tCH_3
150	5.92	0.60	178	3.26	0.99		172	tNH_2
101	2.13	0.23	80	11.75	0.22		90	$tCONH_2$
73	13.32	1.56	71	1.36	1.53			$tCHCH_3$

ν -stretching; δ -in-plane deformation; γ -out-of-plane deformation; τ -twisting; ρ -rocking; ω -wagging; t -torsion; Ring-pyrimidine ring; subscripts: as – asymmetric, s- symmetric.

plane deformation $\gamma\text{C}=\text{O}$ are expected in the regions 625 ± 70 and $540 \pm 80 \text{ cm}^{-1}$ respectively²⁰. The band observed at 738 cm^{-1} in the IR spectrum and 731, 528 (DFT) are assigned as $\text{C}=\text{O}$ deformation modes. The $\text{C}=\text{N}$ stretching skeletal bands²⁴ are observed in the range $1650\text{-}1550 \text{ cm}^{-1}$. For conjugated azines the $\nu\text{C}=\text{N}$ mode is reported²⁵ at 1553 cm^{-1} . According to Socrates²⁶, the $\nu\text{C}=\text{N}$ for semicarbazones is expected in the region $1655\text{-}1640 \text{ cm}^{-1}$ in IR spectrum. For the title compound the band observed at 1662 cm^{-1} in the IR spectrum and at 1672 cm^{-1} in Raman spectrum is assigned as $\nu\text{C}=\text{N}$ mode. The DFT calculations give this mode at 1659 cm^{-1} . Ferraz *et al.*²⁷ reported $\nu\text{C}=\text{N}$ at 1643 cm^{-1} for thiosemicarbazone derivatives. Mangalam and Kurup²⁸ reported $\delta\text{C}=\text{N}$ in the range $1571\text{-}1602 \text{ cm}^{-1}$, for thiosemicarbazone ligands. El-Asmy and Al-Hazmi²⁹ reported $\nu\text{C}=\text{N}$ in the range $1606\text{-}1627 \text{ cm}^{-1}$ for benzophenone-substituted thiosemicarbazones. The IR spectra of the reported thiosemicarbazones show bands in the region $1538\text{-}1647 \text{ cm}^{-1}$ as stretching $\text{C}=\text{N}$ ³⁰⁻³². The NH stretching vibration²⁰ appears as a strong and broad band in the region $3390 \pm 60 \text{ cm}^{-1}$. In the present study, the NH stretching band appeared as a doublet at 3426 and 3314 cm^{-1} in the IR spectrum owing to the Davydov coupling between the neighbouring units. The splitting of about 112 cm^{-1} in the IR spectrum is due to strong intermolecular hydrogen bonding. Further more, the NH stretching wave number is red shifted by 105 cm^{-1} from the computational wave number which indicates the weakening of the N-H bond resulting in proton transfer to the neighbouring oxygen³³. A similar type of splitting observed in acetanilide^{34,35} and N-methylacetamide³⁶ in the stretching band is attributed to the Davydov splitting. El-Asmy and Al-Hazmi²⁹ reported νNH in the region $3138\text{-}3323 \text{ cm}^{-1}$ for benzophenone-substituted thiosemicarbazones and their Ni(II) and Cu(II) complexes. The CNH vibration in which N and H atoms move in opposite direction of carbon atom in the amide moiety appears at 1500 cm^{-1} in Raman and 1493 cm^{-1} theoretically, and the CNH vibration in which N and H atoms move in the same direction of carbon atom in the amide group appears at 1284 cm^{-1} (DFT)^{37,38}. The NH rock in the plane is observed at 1048 cm^{-1} theoretically³⁸. The out-of-plane wagging²⁰ of NH is moderately active with a broad band in the region $790 \pm 70 \text{ cm}^{-1}$ and the band at 730 cm^{-1} (DFT) is assigned as this mode, which is

not pure but contains contributions from other modes. El-Shahawy *et al.*³⁸ reported a value 710 cm^{-1} for this mode.

The C-N stretching vibration²⁰ coupled with the δNH , is active in the region $1275 \pm 55 \text{ cm}^{-1}$. El-Shahawy *et al.*³⁸ observed a band at 1320 cm^{-1} in the IR spectrum as this $\nu\text{C}=\text{N}$ mode. In the present case, the bands at 1320 cm^{-1} in the IR spectrum and 1328 cm^{-1} in Raman spectrum are assigned as this mode. The DFT calculations give the corresponding bands at 1335 and 1284 cm^{-1} . $\nu\text{N}=\text{N}$ has been reported at 1151 cm^{-1} by Crane *et al.*³⁹, 1121 cm^{-1} by Bezerra *et al.*⁴⁰ and 1130 cm^{-1} by El-Behery and El-Twigry⁴¹. In the present case, the band observed at 1123 cm^{-1} (IR), 1130 (Raman) and at 1120 cm^{-1} (DFT) is assigned to the $\delta\text{N}=\text{N}$ mode. The experimental N-N bond length of hydrazine⁴² is reported at 1.449 \AA and the electron diffraction N-N bond length of tetramethylhydrazine⁴³ is reported as 1.401 \AA . In the present case, the N-N bond length is 1.3837 \AA (B3LYP), which is somewhere between the length of an N-N single bond (1.45 \AA) and an N=N double bond (1.25 \AA). For the title compound the bond length $\text{C}_9=\text{N}_8 = 1.2822 \text{ \AA}$ (B3LYP), shows typical double bond characteristics. However, $\text{C}_1-\text{N}_4 = 1.3904 \text{ \AA}$ (B3LYP) and $\text{C}_1-\text{N}_3 = 1.3945 \text{ \AA}$ (B3LYP), bond lengths are shorter than the normal C-N single bond length which is about 1.48 \AA . The shortening of the C-N bonds reveal the effect of resonance in this part of the molecule⁴⁴. Ferraz *et al.*²⁷ reported the bond lengths $\text{N}_8-\text{N}_4 = 1.3815 \text{ \AA}$, $\text{C}_9=\text{N}_8 = 1.3005 \text{ \AA}$, $\text{N}_4-\text{C}_1 = 1.3105 \text{ \AA}$ for thiosemicarbazones metal complexes. Latheef *et al.*⁴⁵ reported the bond lengths N-N 1.3964 , C-N 1.3485 and C-N 1.3175 , 1.2965 \AA which are comparable to that for C=N bond length for copper (II) complexes of thiosemicarbazones⁴⁶. For semicarbazone derivatives, the reported values of $\text{C}_9=\text{N}_8 = 1.2754 \text{ \AA}$ ⁴⁷, 1.2886 \AA ⁴⁸, 1.296 \AA ⁴⁹,



1.303Å⁵⁰, C₁-N₄ = 1.3621Å⁴⁷, 1.3706Å⁴⁸, 1.336 Å⁴⁹, 1.365Å⁵⁰ and C₁-N₃ = 1.3250Å⁴⁷, 1.3281Å⁴⁸, 1.331Å⁴⁹, 1.314 Å⁵⁰.

Seena and Kurup⁵¹ reported the geometrical parameters as N-N 1.3967, C-N=1.2767, 1.3087, 1.3939, N-H 0.818Å, bond angles, C-N-N 115.6°, C-N-N 111.0°, for zinc(II) complexes of salicylaldehyde N(4)-phenyl thiosemicarbazone. For thiosemicarbazone derivatives, Hernandez *et al.*⁵² reported the bond lengths as (XRD) as C₉-N₈ = 1.2844, N₄-C₁ = 1.3544, C₁-N₃ = 1.3424-1.3541Å and the bond angles N₄-N₈-C₉ = 115.0 – 118.6, N₈-N₄-C₁ = 119.8-113.5° and N₄-C₁-N₃ = 120.8°. Dilovic *et al.*⁵³ reported C₁-N₃ = 1.3462, C₁-N₄ = 1.3422 and N₈-C₉ = 1.2862Å. For the title compound, the C₁=O₂ bond length is 1.2221Å and the DFT calculations give the bond angles C₉-N₈-N₄ = 120.7°, N₈-N₄-C₁ = 128.6°, O₂-C₁-N₄ = 125.1, O₂-C₁-N₃ = 122.6°, N₄-C₁-N₃=112.3. The reported values of C₁=O₂ are, 1.2397⁴⁷,

1.2431⁴⁸, 1.25⁵⁴, 1.252⁵⁰ and 1.266Å⁵⁵. For similar derivatives, the reported values are C₉-N₈-N₄=115.4⁴⁷, 118.5⁴⁸, N₈-N₄-C₁ =120.3⁴⁷, N₄-C₁-O₀=120.4⁴⁸, N₄-C₁-N₃=116.0⁴⁸, O₂-C₁-N₃=124.0⁴⁷, 123.6⁹⁴⁸.

The calculated first hyperpolarizability of the title compound is 0.98×10⁻³⁰ esu. The C-N distances in the calculated molecular structure vary from 1.2822-1.3945 Å which are intermediate between those of a C-N single bond (1.48 Å) and a C=N double bond (1.28 Å). Therefore, the calculated data suggest an extended π-electron delocalization over the carbazone moiety⁵⁶ which is responsible for the nonlinearity of the molecule. For thiosemicarbazone complexes, the calculated hyperpolarizabilities are reported in the range 2.6 10⁻³⁰-10.1 10⁻³⁰ esu⁵⁶. We conclude that the title compound is an attractive object for future studies of non linear optical properties.

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