

FTIR, FT-Raman and quantum chemical calculations of 5-chloromethyl-2-oxazolidinone

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Abstract

The optimized molecular structure, vibrational frequencies, corresponding vibrational assignments of the title compound have been investigated experimentally and theoretically using Gaussian09 software package. The geometry optimization has been carried out using HF and DFT levels. The data obtained from vibrational wavenumber calculations are used to assign vibrational bands obtained in IR and Raman spectroscopy of the studied molecule. The calculated infrared intensities and Raman activities are reported. The calculated first hyperpolarizability value shows that the title compound is suitable for nonlinear optical studies. From the HOMO and LUMO analysis, the hardness value of the title compound is 2.868 eV and we conclude that the title compound belongs to hard material.

Key words: oxazolidinone, DFT, hyperpolarizability, Gaussian09.

Introduction

Oxazolidinone functionalized enecarbamates offer unusual opportunities to explore mechanistically versatile systems for the study of conformational, electronic, stereoelectronic and steric effects¹⁻³. Saito *et al.*,⁴ reported the stereoselective photoisomerization of oxazolidinone functionalized enecarbamates. Oxazolidinone derivatives from carboxylic acids have proven to be the dienophiles of choice in many studies concerning chiral Lewis acid catalyzed enantioselective Diels Alder reactions⁵. Due to

the bidentate chelating properties^{6,7} of this type of dienophiles high levels of asymmetric induction have been reported in catalytic studies by various groups⁸⁻¹². The oxazolidinone derivatives to control absolute stereoselection has found wide application in a variety of reactions over the last two decades^{13,14}. They have shown various pharmacological activities in the areas of drug development, antibacterials¹⁵ inhibitors of monoamine oxidase¹⁶, cytokine modulators¹⁷, Sigmareceptors¹⁸, psychotropics, antiallergy agents, antibiotics¹⁹, inter mediates

in the synthesis of renin inhibitors, β -lactam and macrolide antibiotics²⁰, immune suppressants²¹ and in many other applications²². In the present study the FT-IR, FT-Raman and theoretical calculations of the wavenumbers of 5-chloromethyl-2-oxazolidinone are reported.

Experimental

The FT-IR spectrum was recorded using a DR/Jasco FT-IR 6300 spectrometer. The spectral resolution was 2 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.

Computational Details :

Calculations of the title compound were carried out with Gaussian09 software program²³ using the HF/6-31G* and B3LYP/6-31G* basis sets to predict the molecular structure and vibrational wavenumbers. The DFT hybrid B3LYP functional method tends to overestimate the fundamental modes; therefore scaling factors have to be used for obtaining a considerably better agreement with experimental data²⁴. The wavenumber values computed contain known systematic errors and we therefore, have used the scaling factor values of 0.8929 and 0.9613 for HF and DFT basis sets²⁴. The observed disagreement between theory and experiment could be a consequence of the anharmonicity and of the general tendency of the quantum chemical methods to overestimate the force constants at the exact equilibrium geometry. The assignment of the calculated wavenumbers is aided by the

animation option of Gaussview program, which gives a visual presentation of the vibrational modes²⁵.

Results and Discussion

IR and Raman spectra :

The observed IR, Raman and calculated (scaled) wavenumbers and assignments are given in Table 1. The NH stretching vibration²⁶ is expected in the region $3390 \pm 60\text{ cm}^{-1}$. In the present study, the NH stretching band is assigned at 3558 cm^{-1} theoretically (DFT). El Asmy and Al Hazmi²⁷ reported ν_{NH} in the region $3138\text{-}3323\text{ cm}^{-1}$. The CNH vibrations in which N and H atoms move in opposite directions of the carbon atom in the amide moiety appear at 1522 cm^{-1} in the IR spectrum and at 1513 cm^{-1} theoretically (DFT) and the CNH vibrations in which N and H atoms move in the same direction of the carbon atom in the amide group appear at 1249 (IR), 1256 (Raman) and 1245 cm^{-1} (DFT)²⁸⁻³⁰. The out of plane wagging³¹ of NH is moderately active with a broad band in the region $790 \pm 70\text{ cm}^{-1}$ and the band at 731 cm^{-1} (DFT) is assigned as this mode. El Shahawy *et al.*³⁰ reported a value 710 cm^{-1} for this mode. Badawi reported³² the NH vibrational modes at 3315, 1498, 1268 cm^{-1} in the IR spectrum, 3320, 1508, 1264 cm^{-1} in the Raman spectrum and at 3617, 1502, 1256 cm^{-1} theoretically. Panicker *et al.*³³ reported the NH bending modes at 1538, 1220 cm^{-1} in the IR spectrum and at 1558, 1223 cm^{-1} theoretically (DFT). The CN stretching vibration³¹ coupled with δ_{NH} , is moderately to strongly active in the region $1275 \pm 55\text{ cm}^{-1}$. El Shahawy *et al.*³⁰

observed a band at 1320 cm^{-1} in the IR spectrum as the ν_{CN} mode. Yang *et al.*³⁴ reported aromatic CN stretching band at 1359 cm^{-1} . In the present case, the bands at $1208, 1188\text{ cm}^{-1}$ in the IR spectrum and at 1195 cm^{-1} in the Raman spectrum are assigned as this mode. The DFT calculations give the corresponding bands at 1215 and 1184 cm^{-1} .

The aliphatic CCl bonds absorb²⁸ at $830\text{--}560\text{ cm}^{-1}$ and putting more than one chlorine on a carbon atom raises the CCl wavenumber. The CCl_2 stretching mode is reported at around 738 cm^{-1} for dichloromethane and scissoring mode^{28,29} δCCl_2 around 284 cm^{-1} . Arslan *et al.*³⁵ reported ν_{CCl} at 683 cm^{-1} (experimentally) and at $711, 736, 687, 697\text{ cm}^{-1}$ theoretically. The deformation bands of CCl are reported³⁵ at $431, 435, 441$ and 443 cm^{-1} . In the present case the bands at 644 (DFT), 650 (IR) and 651 cm^{-1} (Raman) are assigned as ν_{CCl} bands. The deformation bands of the CCl are assigned below 500 cm^{-1} .

The vibrations of the CH_2 group, the asymmetric stretch $\nu_{\text{as}}\text{CH}_2$, symmetric stretch $\nu_{\text{s}}\text{CH}_2$, scissoring vibration δCH_2 and wagging vibration ωCH_2 appear in the regions $3000 \pm 50, 2965 \pm 30, 1455 \pm 55$ and $1350 \pm 85\text{ cm}^{-1}$, respectively^{28,31}. The DFT calculations give asymmetric and symmetric stretching modes of CH_2 at $3033, 3019$ and $3004, 2940\text{ cm}^{-1}$. The bands observed at $3021, 2955\text{ cm}^{-1}$ in the IR spectrum and at 3024 cm^{-1} in the Raman spectrum are assigned as these modes. The CH_2 deformation band which comes near 1463

cm^{-1} in alkenes²⁸ is lowered to about 1440 cm^{-1} when the CH_2 group is next to a double or triple bond. A carbonyl, nitrile or nitro group each lowers the wavenumber of the adjacent CH_2 group²⁸ to about 1425 cm^{-1} . The band observed at 1397 cm^{-1} in the IR spectrum, 1414 in the Raman spectrum and at $1408, 1364\text{ cm}^{-1}$ (DFT) are assigned as scissoring mode of CH_2 . The CH_2 wagging modes are observed at 1344 cm^{-1} in the IR spectrum, 1341 cm^{-1} in Raman spectrum and the DFT calculations give these modes at $1337, 1275\text{ cm}^{-1}$. The twisting modes and rocking modes are assigned at $1086, 1039\text{ cm}^{-1}$ and $813, 731\text{ cm}^{-1}$ theoretically, which are expected in the regions, 1150 ± 35 and $895 \pm 85\text{ cm}^{-1}$, respectively³¹.

The carbonyl group is contained in a large number of different classes of compounds, for which a strong absorption band due to the C=O stretching vibration is observed in the region³⁶ $1750\text{--}1600\text{ cm}^{-1}$. If a carbonyl group is part of a conjugated system, then the wavenumber of the carbonyl stretching vibration decreases, the reason being that the double bond character of the C=O group is less due to the π -electron conjugation being localized. For the title compound, the stretching C=O mode is seen as a strong band at 1749 cm^{-1} in the IR and the DFT calculations give this mode at 1752 cm^{-1} . The stretching modes of the carbonyl group of the ester part may be lowered in the presence of conjugation³⁷. For the title compound the C=O stretching mode is assigned at 1736 (IR), 1733 (Raman) and at 1745 cm^{-1} (DFT) theoretically. The COC stretching vibration³¹ often considered as the C–O–C asymmetric stretch, appears strongly at 1255

$\pm 60 \text{ cm}^{-1}$, a region in good agreement with that of the $\nu\text{C-O}$ in carboxylic acids ($1250 \pm 80 \text{ cm}^{-1}$) and the symmetric COC stretching mode³¹ in the region $975 \pm 125 \text{ cm}^{-1}$. The band at 842 cm^{-1} given by DFT calculation is assigned as this mode. The $\delta\text{C=O}$ deformation³¹ has been found in the region $710 \pm 80 \text{ cm}^{-1}$ and the band at 695 cm^{-1} (DFT) is assigned to this mode. The $\gamma\text{C=O}$ absorption³¹ is in the range $625 \pm 75 \text{ cm}^{-1}$ and the DFT calculation gives this mode at 688 cm^{-1} . The C-C(=O)-O deformation³¹ rock absorbs weakly to moderately in the region $435 \pm 95 \text{ cm}^{-1}$. The skeletal C-O-C deformation³¹ appears in the region $325 \pm 40 \text{ cm}^{-1}$. The ring deformation modes are also identified and assigned (table 1).

First hyperpolarizability :

Non-linear optics deals with the interaction of applied electromagnetic fields in various materials to generate new electromagnetic fields, altered in wavenumber, phase or other physical properties³⁸. Organic molecules able to manipulate photonic signals efficiently are of importance in technologies such as optical communication, optical computing and dynamic image processing^{39,40}. Many organic molecules, containing conjugated π electrons and characterized by large values of molecular first hyperpolarizabilities, were analyzed by means of vibrational spectroscopy^{39,40}. Analysis of organic molecules having conjugated π -electron systems and large hyperpolarizability using infrared and Raman spectroscopies has evolved as a subject of research⁴¹. The calculated first hyperpolarizability of the title compound

is 1.52×10^{-30} esu. We conclude that the title compound is an attractive object for future studies of non linear optical properties⁴².

In order to investigate the performance of vibrational wavenumbers of the title compound, the root mean square (RMS) value between the calculated and observed wavenumbers were calculated. The RMS values of wavenumbers were calculated using the following expression⁴³.

$$RMS = \sqrt{\frac{1}{n-1} \sum_i^n (v_i^{calc} - v_i^{exp})^2}$$

The RMS error of the observed IR and Raman bands are found to be 27.68, 32.56 for HF and 9.03, 7.79 for DFT methods, respectively. The small differences between experimental and calculated vibrational modes are observed. This is due to the fact that experimental results belong to solid phase and theoretical calculations belong to gaseous phase.

Frontier molecular orbitals :

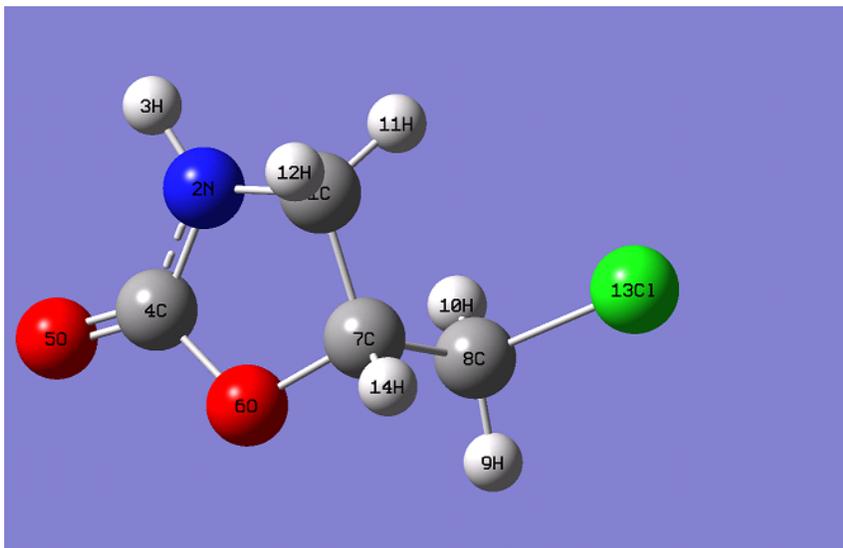
The analysis of the wavefunction indicates that the electron absorption corresponds to a transition from the ground to the first excited state and is mainly described by one electron excitation from the HOMO to LUMO. Both the HOMO and the LUMO are the main orbital taking part in chemical reaction. The HOMO energy characterizes the capability of electron giving; LUMO characterizes the capability of electron accepting⁴⁴. The frontier orbital gap helps to characterize the chemical reactivity, optical polarizability and chemical hardness-softness of a molecule⁴⁵. Surfaces for the frontier orbitals were drawn to understand the bonding scheme of the title compound. The

Table 1. Calculated wavenumbers (scaled), observed IR and Raman bands and assignments

HF/6-31G*			B3LYP/6-31G*			IR $\nu(\text{cm}^{-1})$	Raman $\nu(\text{cm}^{-1})$	Assign- ments
$\nu(\text{cm}^{-1})$	IR _I	R _A	$\nu(\text{cm}^{-1})$	IR _I	R _A			
3520	88.52	73.59	3558	53.98	95.59			νNH
3041	0.86	54.15	3101	2.00	50.44			νCH
2965	12.68	40.53	3033	13.25	48.39			$\nu_{\text{as}}\text{CH}_2$
2955	14.40	129.89	3019	2.22	118.53	3021	3024	$\nu_{\text{as}}\text{CH}_2$
2936	10.49	58.80	3004	11.82	60.32			$\nu_{\text{s}}\text{CH}_2$
2891	23.82	89.05	2940	34.85	112.79	2955		$\nu_{\text{s}}\text{CH}_2$
1741	878.97	7.66	1752	582.26	9.05	1749		$\nu\text{C}=\text{O}$
1516	7.32	10.14	1513	7.95	15.09	1522		δNH
1464	13.95	10.56	1463	11.18	9.02	1472	1451	δCH
1437	15.05	0.57	1408	7.86	0.59		1414	δCH_2
1385	6.63	3.80	1364	12.16	4.14	1379		δCH_2
1365	44.83	5.94	1337	27.95	7.84	1344	1341	ωCH_2
1311	8.65	4.02	1275	6.63	9.12			ωCH_2
1261	28.66	6.46	1245	25.03	2.74	1249	1256	δNH
1231	3.33	6.67	1215	4.50	18.08	1208		νCN
1216	212.68	1.84	1184	140.62	2.60	1188	1195	νCN
1159	6.44	7.75	1150	10.91	6.06			νCOC
1099	7.65	5.85	1086	11.25	5.15	1088	1081	τCH_2
1057	204.28	6.58	1039	52.91	1.21			τCH_2
1041	2.13	4.69	1009	28.95	7.43	1011	1012	νCC
1009	29.32	2.65	955	82.14	5.14		963	νCC
919	53.13	3.44	905	12.88	3.68	899		γCH
896	18.11	9.04	842	74.38	9.48		841	νCOC
813	6.54	15.13	813	3.73	12.14			ρCH_2
739	123.13	1.06	731	32.22	3.85			$\omega\text{NH}, \rho\text{CH}_2$
705	14.97	3.69	695	42.31	6.03	706		$\delta\text{C}=\text{O}$
695	0.58	14.92	688	5.57	17.23	683		$\gamma\text{C}=\text{O}$
650	83.91	17.02	644	46.97	12.97	650	651	νCCl

545	170.22	2.74	515	149.01	3.27	533	524	δ Ring
492	9.67	2.36	481	4.45	1.73			δ CCl
406	3.91	1.64	386	1.52	0.87			γ Ring
294	4.98	7.33	315	8.62	5.61			γ CCl
212	10.30	1.92	213	11.57	3.07		219	δ Ring
143	7.70	0.06	149	2.55	0.46			γ Ring
87	12.30	0.63	109	9.40	0.63			tC=O
17	1.52	0.39	60	2.36	0.81			tCH2

as-asymmetric; s-symmetric; ν -stretching; δ -in-plane deformation; ρ -rocking; τ -twisting; t-torsion.



calculated HOMO and LUMO energies are -8.259 and -2.523 eV. The chemical hardness and softness of a molecule is a good indication of the chemical stability of the molecule. From the HOMO-LUMO energy gap, one can find whether the molecule is hard or soft. The molecules having large energy gap are known as hard and molecules having a small energy gap are known as soft molecules. The soft molecules are more polarizable than the hard ones because

they need small energy to excitation. The hardness value⁴⁴ of a molecule can be determined as $\eta = (-\text{HOMO} + \text{LUMO})/2$. The value of η of the title molecule is 2.868 eV. Hence we conclude that the title compound belongs to hard material.

Conclusion

The optimized molecular structure,

vibrational frequencies, corresponding vibrational assignments of the title compound have been investigated experimentally and theoretically using Gaussian09 software package. The geometry optimization has been carried out using HF and DFT levels. The data obtained from vibrational wavenumber calculations are used to assign vibrational bands obtained in IR and Raman spectroscopy of the studied molecule. The calculated infrared intensities and Raman activities are reported. The calculated first hyperpolarizability value shows that the title compound is suitable for nonlinear optical studies.

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