

Normal Coordinate Analysis and Spectral Analysis of Cyclohexanone Oxime

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FTIR and FTR spectra of cyclohexanone oxime have been recorded in the regions 4000-200 and 4000-30 cm^{-1} , respectively. The vibrational analysis has been carried out by assuming C_s symmetry. The observed frequencies were assigned to various modes of vibrations on the basis of intensity, frequencies from allied molecules and normal coordinate calculations. The potential energy distribution associated with normal modes are also reported here. The assignments of fundamental vibrational frequencies for cyclohexanone oxime agree with the calculated frequencies. The different chemical environments of the protons were ascertained using ^1H NMR spectra and the purity of the compound was confirmed by mass spectral data.

Key Words: Vibrational spectra, Normal coordinate calculation, Cyclohexanone oxime.

INTRODUCTION

Cyclohexanone oxime, a derivative of cyclohexanone is a white crystalline solid that can be crystallized as prisms from hydrocarbon solvents with melting point 90.5 °C and boiling point 204 °C, sublimates at room temperature. This chemical compound is stable under normal laboratory conditions and the most important commercial derivative of cyclohexanone. Cyclohexanone oxime is an intermediate in the preparation of caprolactam, which is used in nylon manufacture. It is also used as a therapeutic agent. NMR spectra of some oximes were measured at natural isotopic abundance in pyridine and acetonitrile solutions¹. The temperature dependence of the FT-IR spectra of absorbed cyclohexanone oxime was studied on pentasil zeolite². Thermodynamic properties like heat of crystalline capacities and liquid cyclohexanone oxime were measured by vacuum adiabatic calorimetry (6-300 K) and by the triple heat bridge method (300-450 K)³. The rearrangement of cyclohexanone oxime to ϵ -caprolactam was investigated over heterogeneous catalysts⁴. Jain *et al.*⁵ reported the mechanism of reaction of impurities such as cyclohexanol, cyclohexanone, aniline and cyclohexanone oxime, during the course of polymerisation of caprolactam. This indicates that cyclohexanone oxime's application in the manufacture of nylon. A simplified industrial route for the synthesis of cyclohexanone oxime an

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intermediate in the caprolactam process was described by Roffia *et al.*⁶. This chemical compound was employed as an oxidant in redox polymerization⁷. Talukdar *et al.*⁸ reported the use of solar energy for the photonitrosation of cyclohexanone for the production of cyclohexanone oxime hydrochloride, an intermediate for the manufacture of caprolactam. In the present work, the spectral analysis of cyclohexanone oxime has been reported. The aim of this work is to propose assign all the vibrational frequencies for cyclohexanone oxime using the normal coordinate analysis through FT-infrared and FT-Raman spectroscopy.

EXPERIMENTAL

FTIR spectrum of cyclohexanone oxime was recorded on Bruker IFS 66V FTIR spectrophotometer in the region 4000-200 cm^{-1} . FT Raman spectrum of the same compound was also recorded on the same instrument with FRA 106 Raman module equipped with Nd: YAG laser source operating at 1.06 μm line with a scanning speed of 30 $\text{cm}^{-1} \text{min}^{-1}$ of spectral width 20 cm^{-1} . The frequencies for all sharp bands were accurate to $\pm 1 \text{ cm}^{-1}$. The ^1H and ^{13}C NMR spectra of cyclohexanone oxime were recorded using Jeol 500 MHz.

Mass spectral analysis: The mass spectra showed a parent molecular ion peak at $m/z = 113.0$ ($M + 1$ peak), which losses oxime -OH and produces a peak at $m/z = 96$ ($M + 1$ peak). Next the ring broke down into acetonitrile and *n*-butane in turn confirmed by the peaks at $m/z = 41$ (100 %, base peak) and $m/z = 56$, respectively. The *n*-butane group further decomposes to ethyl radical which appeared at $m/z = 27$.

Theoretical considerations: The molecular symmetry of the molecule helps to determine and classify the actual number of fundamental vibrations of the system. The observed spectrum is explained on the basis of C_s point group symmetry. The 51 optically active fundamental vibrations are distributed as $\Gamma_{\text{vib}} = 35a'$ (in-plane) + 16a'' (out-of-plane).

All the modes are active in both Raman and infrared. The assignments have been made on the basis of relative intensities, magnitudes of the frequencies and polarization of the Raman lines. The vibrational assignment was made in terms of the potential energy distribution, which was obtained from the evaluated constants.

Normal coordinate analysis: The normal coordinate calculations have been performed to obtain vibrational frequencies and the potential energy distribution for the various modes. In the normal coordinate analysis, the potential energy distribution plays an important role for the characterization of the relative contributions from each internal coordinates to the total potential energy associated with particular normal coordinate of the molecule.

The normal coordinate analysis is necessary for complete assignment of the vibrational frequencies of larger polyatomic molecules and for quantitative description of the vibrations. The values of bond-length and bond-angles have been taken from allied molecules and Sutton table⁹. Internal co-ordinates for the out-of-plane torsional vibrations are defined as recommended by IUPAC. The simple valence

force field has been adopted for both in-plane and out-of-plane vibrations. The normal coordinate calculations have been performed using the program of Fuhrer *et al.*¹⁰. The initial set of force constants have been taken from the related molecules.

Potential energy distribution: To check whether the chosen set of assignments contribute maximum to the potential energy associated with normal coordinates of the molecules, the potential energy distribution (PED) has been calculated using the relation

$$PED = \frac{F_{ii} L_{ik}^2}{\lambda_k} \quad (1)$$

where F_{ii} are the force constants defined by damped least square technique, L_{ik} is the normalized amplitude of the associated element (i, k) and λ_k the eigen value corresponding to the vibrational frequency of the element k. The PED contribution corresponding to each of the observed frequencies over 10 % are alone listed in the present work.

RESULTS AND DISCUSSION

The observed frequencies along with their relative intensities of cyclohexanone oxime and probable assignments are presented in Table-1.

TABLE-1
OBSERVED, CALCULATED FREQUENCIES (cm⁻¹), VIBRATIONAL ASSIGNMENTS
AND POTENTIAL ENERGY DISTRIBUTION OF CYCLOHEXANONE OXIME

Sps.	Observed		Calcd. wave number	Assignment	PED (%)
	freq./intensity Infrared	Raman			
a'	3187 s	3180 w	3181	O-H stretching	92 v(O-H)
a'	–	2988 w	2982	C-H stretching	86 v(C-H)
a'	2977 s	–	2969	C-H stretching	94 v(C-H)
a'	–	2962	2958	C-H stretching	92 v(C-H)
a'	–	2938 s	2934	C-H stretching	89 v(C-H)
a'	2925 s	–	2921	C-H stretching	90 v(C-H)
a'	–	2900 m	2890	C-H stretching	82 v(C-H) + 14 v(C-C)
a'	2889 s	–	2881	C-H stretching	88 v(C-H)
a'	–	2857 m	2849	C-H stretching	76 v(C-H) + 16 v(C-C)
a'	2843 s	–	2837	C-H stretching	84 v(C-H)
a'	–	2831 w	2828	C-H stretching	86 v(C-H)
–	2668	–	–	1331 + 1319	–
a'	1669 s	1663s	1664	C = N stretching	71 v(C-N) + 19 v(C-C) + 10 v(C-H)
a'	1480 s	1480 m	1475	C-H in plane bending	84 β(C-H)
a'	1458 m	1450 vs	1448	C-H in plane bending	89 β(C-H)
a'	1436 m	1436 s	1431	C-H in plane bending	76 β(C-H) + 21 β(C-C)
a'	1350 w	–	1341	C-H in plane bending	83 β(C-H)
a'	–	1339 w	1332	C-H in plane bending	91 β(C-H)
a'	1331 w	1325 s	1319	C-H in plane bending	89 β(C-H)

a'	1319 w	1319 s	1308	C-H in plane bending	70 β (C-H) + 26 β (C-C)
a'	–	1264 w	1261	C-H in plane bending	86 β (C-H)
a'	1250 m	–	1252	C-H in plane bending	84 β (C-H)
a'	–	1239 s	1231	C-H in plane bending	69 β (C-H) + 28 β (C-C)
a'	1225 m	–	1219	C-C stretching	79 ν (C-C)
a'	–	1214 s	1208	C-C stretching	82 ν (C-C)
a'	1138 w	1138 w	1131	C-C stretching	88 ν (C-C)
a'	1110 m	1100 s	1102	C-C stretching	76 ν (C-C)
a'	1095 vw	–	1081	C-C stretching	70 ν (C-C) + 26 ν (C-H)
a'	1088 w	1084 w	1079	C-C stretching	68 ν (C-C) + 22 ν (C-H)
a'	1088 w	1084 w	–	CCC in plane bending	–
a'	1068 vw	1063 vs	1061	CCC in plane bending	83 β (C-C-C)
a'	1019 vw	1019 s	1011	CCC trigonal bending	92 β (C-C-C)
a'	1019 vw	1019 s	–	N-OH stretching	–
a'	995 vs	995 m	992	CCC in plane bending	89 β (C-C-C)
a'	995 vs	995 m	–	CCC ring breathing	–
a''	950 s	956 w	949	C-H out of plane bending	74 η (C-H)
a''	–	931 m	928	C-H out of plane bending	79 η (C-H)
a''	919 w	920 vw	920	C-H out of plane bending	81 η (C-H)
a''	900 m	900 m	892	C-H out of plane bending	84 η (C-H)
a''	–	868 vw	860	C-H out of plane bending	71 η (C-H)
a''	850 w	–	838	C-H out of plane bending	61 η (C-H) + 30 η (C-C)
a''	–	838 m	831	C-H out of plane bending	74 η (C-H)
a''	794 w	–	788	C-H out of plane bending	57 η (C-H) + 32 η (C-C)
a'	775 w	775 vs	762	β (in plane bending) C = N-OH oxime	45 β (C=N-OH) + 20 β (C-C) + 21 β (C-H)
a''	656 w	656 w	641	η (out of plane bending) C = N-OH oxime	47 η (C=N-OH) + 16 η (C-H) + 22 η (C-C)
a''	656 w	656 w	–	C-H out of plane bending	–
a''	481 m	482 vw	470	CCC out of plane bending	61 η (C-C-C) + 22 η (C=N-OH)
a''	481 m	482 vw	–	C-H out of plane bending	–
a''	438 m	438 m	428	CCC out of plane bending	59 η (C-C-C) + 30 η (C=N-OH)
a''	344 w	350 s	341	N-O-H out of plane bending	41 η (N-OH) + 29 η (C-N) + 12 η (C-C)
a''	281 w	288 vs	269	CCC out of plane bending	54 η (C-C-C) + 26 η (C-H)
a''	250 vw	–	239	CCC out of plane bending	58 η (C-C-C) + 22 η (C-H)

a': in-plane vibrations, a'': out-of plane vibrations, w: weak, m: medium, s: strong, vw: very weak, vs: very strong.

C-H Stretching: In large numbered rings such as cyclohexane, the C-H stretching absorptions are usually observed below 3000 cm^{-1} . In the present case, the absorption band observed at 2977, 2925, 2889 and 2843 cm^{-1} in the IR spectrum and 2988, 2962, 2938, 2900, 2857 and 2831 cm^{-1} in the Raman spectrum are assigned to the C-H stretching present in the cyclohexane ring. The weak and strong wave numbers correspond to symmetric and antisymmetric vibrations of the C-H bond. The calculated wave numbers agree with the observed frequencies. The present conclusion is in

agreement with the literature values¹¹⁻¹³. The PED calculation for C-H stretching indicates that all are pure modes except at the calculated frequency at 2890 and 2849 cm^{-1} which are mixed modes with little contributions due to C-C stretching.

O-H Stretching: In the infrared, O-H stretching band is of medium to strong intensity although it may be broad. However, in Raman spectra, the band is generally weak. The O-H stretching of the cyclohexanone oxime is assigned to 3187 cm^{-1} which agrees with the calculated frequency¹⁴⁻¹⁶ at 3181 cm^{-1} .

C=N Stretching: For oximes, C=N stretching band occurs in the region 1690-1620 cm^{-1} . In the present case, it is assigned to strong infrared at 1669 cm^{-1} which agrees with calculated frequency at 1664 cm^{-1} and literature value¹⁷.

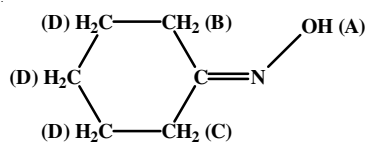
C-C Stretching: The skeletal vibration of alkane is often weak in infrared and usually of weak to medium intensity in Raman spectra. The C-C stretching absorptions occur in the region 1260-700 cm^{-1} . Thus bands observed at 1225, 1214, 1138, 1110, 1095 and 1088 cm^{-1} are assigned to six C-C stretching vibrations and they are in good agreement with the calculated frequencies.

In-plane and out-of-plane bendings

C-H Bending: The C-H in plane bending vibration in cyclohexane rings is usually observed in the region between 1400-1000 cm^{-1} which is normally weak while the C-H out of plane vibrations occurring between 1000-700 cm^{-1} is normally strong. With this observation, the bands at 1480, 1458, 1436, 1350, 1339, 1331, 1319, 1264, 1250 and 1239 cm^{-1} are assigned to C-H in plane bending while the bands observed at 950, 931, 919, 900, 868, 850, 838, 794, 656 and 482 cm^{-1} are assigned to C-H out of plane bending vibrations. These bending vibrations due to the C-H bond well agree with the calculated frequencies as shown in Table-1 and with the literature values^{18,19}.

Ring breathing: The C-C-C trigonal bending and C-C-C ring breathing vibrations are assigned to 1019 and 995 cm^{-1} , respectively which agree with calculated values at 1011 and 992 cm^{-1} . This conclusion is in good agreement with the literature values²⁰.

¹H NMR analysis: ¹H NMR spectra of the compound consists of multiplets in the range 1-3 ppm, shows that the ring protons are not equal. Since the protons on {B} carbon are *cis* to oxime -OH they appeared at $\delta = 2.50$ ppm down field (diamagnetic shift) where as the *trans* protons on {C} carbon resonates at $\delta = 2.22$ ppm. The rest 6 proton of {D} carbon resonates at $\delta = 1.74$ ppm (paramagnetic shift). All the three signals were splitted into triplets by the neighbouring two protons. The -OH proton appeared as a board signal at $\delta = 8.9$ ppm.



Structure of cyclohexanone oxime

Similar trend was observed with ^{13}C NMR also. Except carbon all other carbons appeared in the range between 20-40 ppm. Due to electron withdrawing nature of N carbon (A) resonators at down field *i.e.* at $\delta = 160$ ppm.

Conclusion

A complete vibrational band assignment of cyclohexanone oxime has been carried out using infrared and Raman spectra on the basis of C_s point group symmetry. The PED calculation regarding the normal modes of vibration provide a strong support for the frequency assignment on the highly complex molecule. A satisfactory spectral analysis has been made for the cyclohexanone oxime using NMR and mass spectra. An NMR spectrum shows that the ring protons are not equal. Mass spectra shows that the molecular mass peak of the compound.

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