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FTIR and FT Raman Spectra, Vibrational Assignment and Analysis of 1,2-Cyclohexanedione

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FTIR and FT Raman spectra of 1,2-cyclohexanedione 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 the normal coordinate calculations. The potential energy distributions associated with normal modes are also reported. The assignment of fundamental vibrational frequencies for 1,2-cyclohexanedione agree well with calculated frequencies.

Key Words: Vibrational spectra, Normal coordinate calculation, 1,2-Cyclohexanedione.

INTRODUCTION

1,2-Cyclohexanedione, a derivative of cyclohexane appears in pale yellow solid. This compound has melting point 35-38 ºC and it is moderately soluble in water. This compound is also used as an analytical reagent for nickel. The spectra of the diketone has been investigated by the technique of low-energy variable-angle electron energy-loss spectroscopy[1]. Ravindranath *et al.*[2] reported Raman intensity analysis of cyclic molecules-cyclohexane. Sciesinska[3] recorded far infrared spectra of cyclohexane C_6H_{12} in the frequency range of 650-100 cm^{-1} for the phases I and II at various temperatures. The reflection-absorption infrared spectrum of cyclohexane absorbed on Pt(III) has been recorded using a fourier transform spectrometer[4].

Hence, the present investigation has been undertaken to provide complete spectroscopic information and vibrational analysis of 1,2-cyclohexanedione through FTIR and FT Raman spectroscopy. The normal coordinate calculation has also been performed to check the validity of the present assignment.

EXPERIMENTAL

FTIR spectrum of 1,2-cyclohexanedione was recorded on Bruker IFS 66V FTIR spectrometer 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

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cm^{-1} min^{-1} of spectral width 20 cm^{-1}. The frequencies for all sharp bands were accurate to ± 1 cm^{-1}. The recorded spectrum of 1,2-cyclohexanedione is shown in the Fig. 1.

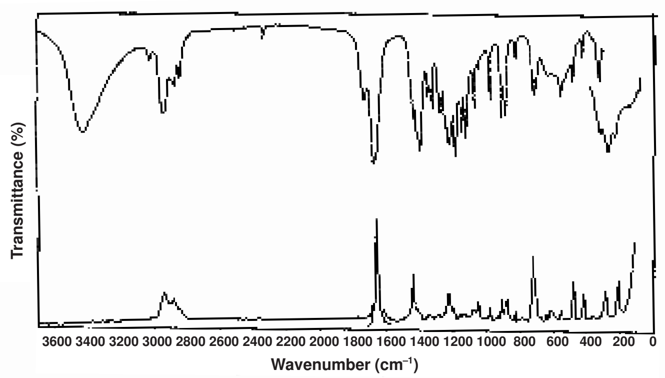

Fig. 1. FTIR and FTR spectra of 1,2-cyclohexanedione

Theoretical considerations: The symmetry possessed by a 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 42 fundamental vibrations are distributed as $\Gamma_{vib} = 29a' + 13a''$.

All the vibrations are both infrared and Raman active. The observed frequencies have been assigned to various modes of vibration on the basis of intensity, frequency and from the allied molecules. The normal coordinate calculations have also been employed for this purpose. The initial set of force constants are taken from allied molecules and small alterations are made in few constants to obtain a close fit between the observed and calculated frequencies. The potential energy distributions associated with each vibrational mode are calculated and thereby the magnitudes of mixing up of various skeletal frequencies are investigated.

Normal coordinate analysis: With the modified computer program developed in this laboratory[5] the normal coordinate analysis for this compound was carried out using Wilson's F-G matrix method. The simple general valence force field was adopted for both in plane and out of plane vibrations. The structural parameters are taken from related molecules and Sutton's Table-1[6]. The initial set of force constants were refined by keeping few interaction constants fixed throughout the refinement process. The assignment to all in plane and out of plane fundamentals are made on the basis of intensities of Raman and IR bands, normal coordinate analysis and on comparison with those of similar 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:

$$\mathrm{PED} = \frac{F_{ii} L_{ik}^2}{\lambda_\kappa}$$

where F_{ii} are the force constants defined by damped least square technique, L_{ik} 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 1,2-cyclohexanedione and probable assignments are presented in the Table-1. The assignment of frequencies has been made as follows.

C-H Stretching: The strong IR band at 2942 cm^{-1}, weak Raman at 2931 and 2914 cm^{-1}, medium IR band at 2900 cm^{-1}, weak Raman band at 2882 cm^{-1}, medium IR band medium at 2869 cm^{-1}, weak IR and Raman at 2850 cm^{-1} and medium IR band at 2838 cm^{-1} have been assigned to C-H stretching vibrations. The calculated wave numbers 2936, 2920, 2909, 2902, 2881, 2858, 2844 and 2828 cm^{-1} agree quite well with the observed frequencies and literature values[7]. The PED calculation for C-H stretching modes reveal that all are pure modes except at the assigned frequency of 2869 cm^{-1} which is a mixed mode with 78 % contribution due to C-H stretching and a little contribution of about 10 % due to C-C stretching.

C=O Stretching: The C=O stretching bands of 1,2-cyclohexanedione have been assigned at 1731 and 1675 cm^{-1} which agree with the calculated values 1726 and 1669 cm^{-1}. The PED obtained for C=O stretching at 1669 cm^{-1} (calculated) shows that there is 81 % contribution from C=O stretching mode along with 15 % of contribution from C-C stretching mode.

C-C Stretching: Six C-C stretching vibrations of 1,2-cyclohexanedione have been assigned as strong IR band at 1250 cm^{-1}, strong IR at 1225 cm^{-1}, strong IR at 1188 cm^{-1} and weak Raman at 1081 cm^{-1}, strong IR at 1144 cm^{-1} and strong IR at 1122 cm^{-1}. They all agree with the calculated frequencies 1251, 1220, 1176, 1138, 1111 and 1069 cm^{-1}. The PED for C-C stretching at 1069 cm^{-1}. The PED for C-C stretching at 1069 cm^{-1} show that it is a mixed mode with a little contribution from C-H stretching (12 %).

In-plane and out of plane bendings: Eight C-H in-plane bendings are assigned to medium IR at 1468 cm^{-1}, strong IR 1449 cm^{-1}, weak Raman 1438 cm^{-1}, very strong IR 1400 cm^{-1}, medium IR 1363 cm^{-1}, medium IR 1338 cm^{-1}, medium IR 1325 cm^{-1} and strong IR 1275 cm^{-1} which agree closely with the calculated wave numbers 1460, 1438, 1426, 1406, 1356 1328, 1320 and 1276 cm^{-1}. These vibrations appear in the expected range and find support from literature values[8]. The PED calculation for C-H in plane bending shows that all are pure modes except at 1460 and 1276 cm^{-1} where there are contributions from C-C in plane bending (16 %) and C=O in plane bending (19 %) also.

Eight C-H out of plane vibrations are assigned to 1035 cm^{-1} (very weak Raman), 1018 cm^{-1} (very weak Raman), 980 cm^{-1} (medium IR), 900 cm^{-1} (strong IR), 882 cm^{-1} (strong IR), 869 cm^{-1} (very weak Raman), 856 cm^{-1} (very weak Raman), 819

TABLE-1
OBSERVED, CALCULATED FREQUENCIES (cm^{-1}), VIBRATIONAL ASSIGNMENTS AND POTENTIAL ENERGY DISTRIBUTION OF 1,2-CYCLOHEXANEDIONE

Sps.	Observed freq./intensity		Calcd. wave number	Assignment	% PED
	Infrared	Raman			
a′	2942 s	–	2936	C-H stretching	94 ν(C-H)
a′	–	2931 w	2920	C-H stretching	91 ν(C-H)
a′	–	2914 vw	2909	C-H stretching	89 ν(C-H)
a′	2900 m	–	2902	C-H stretching	90 ν(C-H)
a′	–	2882 vw	2881	C-H stretching	93 ν(C-H)
a′	2869 m	–	2858	C-H stretching	78 ν(C-H) + 12 ν(C-C)
a′	2850 vw	2850 vw	2844	C-H stretching	88 ν(C-H)
a′	2838 m	–	2828	C-H stretching	86 ν(C-H)
-	2331 vw	–	–	1188 + 1144	–
a′	1731 m	–	1726	C=O stretching	86 ν(C=O)
a′	1675 vs	1675 vs	1669	C=O stretching	81 ν(C=O) + 15 ν(C-C)
a′	1468 m	–	1460	C-H in plane bending	74 β(C-H) + 18 β(C-C)
a′	1449 s	–	1438	C-H in plane bending	29 β(C-H)
a′	–	1438 w	1426	C-H in plane bending	88 β(C-H)
a′	1400 vs	–	1406	C-H in plane bending	81 β(C-H)
a′	1363 m	–	1356	C-H in plane bending	90 β(C-H)
a′	1338 m	1338 m	1328	C-H in plane bending	86 β(C-H)
a′	1325 m	–	1320	C-H in plane bending	79 β(C-H)
a′	1275 s	1282 vw	1276	C-H in plane bending	76 β(C-H) + 10 β(C=O)
a′	1250 s	1250 vw	1251	C-C stretching	86 ν(C-C)
a′	1225 s	1221 w	1220	C-C stretching	91 ν(C-C)
a′	1188 s	1195 vw	1176	C-C stretching	89 ν(C-C)
a′	1144 s	1145 vw	1138	C-C stretching	94 ν(C-C)
a′	1122 s	1125 vw	1111	C-C stretching	96 ν(C-C)
a′	–	1081 vw	1069	C-C stretching	87 ν(C-C) + 12 ν(C-H)
a′	1068 m	–	1054	CCC in plane bending	81 β(C-C) + 11 β(C-H)
a′	1046 w	–	1044	CCC trigonal bending	88 β(C-C-C)
a″	–	1035 vw	1031	C-H out of plane bending	74 η(C-H)
a″	–	1018 vw	1008	C-H out of plane bending	79 η(C-H)
a′	980 m	981 vw	985	CCC ring breathing	89 β(C-C-C)
a″	–	931 vw	928	C-H out of plane bending	81 η(C-H)
a″	900 s	900 w	891	C-H out of plane bending	69 η(C-H) + 18 η(C-C)
a″	882 s	–	878	C-H out of plane bending	83 η(C-H)
a″	–	869 vw	861	C-H out of plane bending	88 η(C-H)
a″	–	856 vw	842	C-H out of plane bending	86 η(C-H)
a″	819 w	820 vw	820	C-H out of plane bending	90 η(C-H)
a′	713 w	713 m	702	C=O in plane bending	84 β(C=O)
a′	700 m	700 w	696	C=O in plane bending	86 β(C=O)
a″	–	638 vw	631	C=O out of plane bending	81 η(C=O)

a″	618 m	613 vw	608	C=O out of plane bending	80 η(C=O) + 19 η(C-H)
a″	544 s	544 vw	538	C-C-C out of plane bending	79 η(C-C-C) + 21 η(C-H)
a″	475 m	475 w	471	C-C-C out of plane bending	86 η(C-C-C)
a″	419 w	419 w	411	C-C-C out of plane bending	82 η(C-C-C)

a′: in-plane vibrations, a″: out-of plane vibrations, abbreviations used: w: weak, m: medium, s: strong, vw: very weak, vs: very strong.

cm^{-1} (weak IR), which agree with calculated wave numbers 1031, 1008, 985, 928, 891, 878, 861, 842 and 820 cm^{-1}. The PED for C-H out of plane bendings indicates all are pure mode except at 891 cm^{-1} (calculated) where there is a little contribution from C-C out of plane bending (18 %).

C=O in plane bendings have been assigned to medium Raman at 713 cm^{-1} and medium IR at 700 cm^{-1} which agree quite well with the calculated values 702 and 696 cm^{-1}. Similarly C=O out of plane bendings are assigned to weak Raman at 638 cm^{-1} and medium at IR 618 cm^{-1} which agree with the calculated values 631 and 608 cm^{-1}.

C-C-C in plane bending vibration is assigned to medium IR at 1068 cm^{-1} which agree with calculated value 1054 cm^{-1}. C-C-C out of plane vibrations are assigned to strong IR band at 544 cm^{-1}, medium IR band at 475 cm^{-1} and weak Raman at 419 cm^{-1} which agree well with calculated values 538, 471 and 419 cm^{-1}.

C-C-C ring breathing and trigonal bending: C-C-C ring breathing and trigonal bending are assigned to IR band at 980 and at 1046 cm^{-1} which agree well with calculated values 985 and 1044 cm^{-1}.

Conclusion

A complete vibrational spectra and analysis has been reported in the present work for the first time for 1,2-cyclohexanedione. The close agreements between the observed and calculated frequencies confirm the validity of the present assignment.

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