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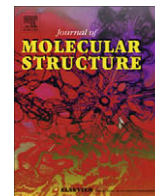**16** PUBLICATIONS   **91** CITATIONS

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Keto–enol tautomers of 1,2-cyclohexanedione in solid, liquid, vapour and a cold inert gas matrix: Infrared spectroscopy and quantum chemistry calculation

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ABSTRACT

Fourier transform infrared (FTIR) spectroscopy of 1,2-cyclohexanedione (CHD) has been studied with the neat sample, low-pressure vapour, CCl_4 solution and in cold N_2 matrix. The matrix-isolation spectrum has been assigned exclusively in terms of transitions of the enol tautomer, that is stabilized by an intramolecular $O \cdots H$—O hydrogen bond (HB). The vibrational fundamentals of the diketo tautomer appear weakly in the spectra of CCl_4 solution and vapour. On the other hand, the spectrum of the neat sample shows significant population of the diketo tautomer. Thus the intermolecular interactions, which are dominant in the neat sample, stabilize the diketo form. The predictions of electronic structure calculations by B3LYP/6-311++G(d,p) and MP2/cc-pVTZ methods are found to be consistent with the measured tautomeric distribution in the cold inert gas matrix. The larger dipole moment of the diketo tautomer (5.61 D) compared to enol form (3.60 D) is proposed to be responsible for stability of the former in the neat sample. The vibrational fundamentals predicted by anharmonic calculation at B3LYP/6-311++G(d,p) level display excellent agreement with measured frequencies. The proposed assignments are further corroborated by noting the deuterium isotopic shifts of different bands and their predicted shifts by the same theoretical methods.

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1. Introduction

This paper is concerned with infrared spectroscopic probing of the keto–enol tautomers of 1,2-cyclohexanedione (CHD) in a cold inert gas matrix, in the vapour phase, in CCl_4 solution and in the neat solid. The 1,2-diketo functional group in a six-membered ring system is an important structural unit found in a number of biologically significant molecules and important also from synthetic viewpoints. The structural unit is considered to be the active site of the anticancer drug Quassinoid Bruceantin [1,2], and anti-tumor steroid 4-hydroxy-androst-4-ene-3,17-dione [3]. A small member of this family, 3-methyl-1,2-cyclohexanedione, is considered to be responsible for coffee aroma [4]. In all cases, there are equilibria between the keto and enol tautomers of the respective molecules, and only the enol forms are functionally active. The preference for the enol tautomer of the structural unit is responsible for success of a large number of important reactions, e.g., benzilic acid rearrangement, Michael reaction, Claisen rearrangement and several photochemical reactions.

In the vapour phase, the tautomeric preference of CHD has been studied in the recent past by a number of powerful spectroscopic methods. For example, using electron energy loss spectroscopy Francis et al. concluded that CHD exists exclusively in enol tautomeric form in the gas phase, and the tautomer is stabilized under the isolated condition by an intramolecular O—H$\cdots$O=C hydrogen bond [5]. Bouchoux et al. arrived to similar conclusion performing the ion cyclotron resonance mass spectrometry measurement [6]. Shen et al. performed electron diffraction measurement of CHD vapour [7] and the enol tautomeric form was proposed to be the dominant species, although the presence of a small fraction of diketo tautomer was not fully ruled out. In contrast to the conclusions of these experimental studies the electronic structure calculation by MP2/6-311G(d,p) method predicts significant stability of the diketo tautomer with the keto–enol population ratio of ~0.72 [7].

On the other hand, although a vibrational spectroscopic method is very sensitive in distinguishing the keto–enol tautomers because of the large difference in frequencies associated with the two functional groups, to our knowledge no systematic vibrational spectroscopic study of CHD has been reported till date. Here we have studied the infrared spectra of the molecule in different media and temperatures, and monitored the change in relative population of the tautomers. The electronic structure calculations were performed at different levels of theory to interpret the measured spectra.

2. Materials and methods

2.1. Experimental

CHD was procured from Aldrich and used as supplied. The FTIR spectra were recorded using a Bruker IFS66S Fourier transform
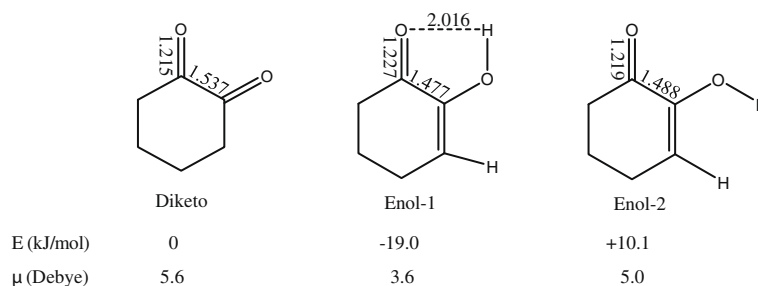
Fig. 1. Optimized structures, relative energies and dipole moments of the diketo and two enol tautomers of CHD calculated at MP2/cc-pVTZ level of theory.

infrared spectrometer equipped with a deuterated triglycine sulphate (DTGS) detector and a KBr beam splitter. The spectral resolution of the spectrometer throughout the measurements was 1 cm^{-1}. The spectrometer compartment was continuously purged with dry N_2 to remove water vapour and CO_2. For matrix isolation studies, a gas mixture of sample vapour and ultrahigh pure nitrogen (N_2) was condensed onto a thin KBr window cooled at ~8 K temperature by a closed cycle helium refrigerator (Advanced Research Systems, Inc., Model No. DE202). The spectra were recorded with matrices generated from gas mixtures containing different partial pressure of the sample vapour and nitrogen. Care was taken to avoid self condensation of the sample molecules in the matrices.

To record the FTIR spectrum of CHD vapour, a low-pressure multi-pass gas cell (Bruker Optics) was used. The effective optical path length of the cell is 8 m. The spectra were recorded with an instrument resolution of 1 cm^{-1}, and partial pressure of the sample in the gas cell was ~10^{-3} torr. To record the spectra at different temperatures, the cell was heated in the range of 22–70 °C by a home-made temperature controller. A solid state diode sensor was used to monitor the temperature inside the cell, and the precision of the displayed temperature was ±0.1 °C.

The FTIR spectrum of the neat CHD sample at room temperature was recorded using the attenuated total reflection (ATR) mode of a compact commercial spectrometer, (Bruker Optics, model: Alpha).

A home-made solution cell consisting of a pair of KBr windows and a Teflon spacer of 1 mm thickness was used for the solution phase measurement. Spectra at different temperatures were recorded by a home-made variable temperature cell of pathlength 1.5 mm.

2.2. Theoretical calculation

The geometries of the three possible tautomers of CHD (Fig. 1) were optimized by B3LYP and MP2 theoretical methods using 6-311++G(d,p) basis set. At MP2 level, calculation was also performed using correlation consistent cc-pVTZ basis set. The gas phase infrared spectra of the tautomers were calculated using the same theoretical methods in harmonic approximation. A scale factor of 0.975 was used on the vibrational frequencies predicted by MP2/cc-pVTZ method to correlate with the experimentally observed vibrational fundamentals. The required scale factor for the

frequencies predicted by B3LYP/6-311++G(d,p) method is found to be 0.98. The frequencies for infrared fundamentals of the vibrational modes of both the tautomers were also calculated by anharmonic method at B3LYP/6-311++G(d,p) level, and we show below that these predictions agree more satisfactorily with the measured frequencies. All calculations reported here were carried out using Gaussian 03 program package [8].

3. Results and discussion

3.1. Relative stability of the tautomers

The relative energies and thermodynamic parameters of the diketo and two enol tautomers (enol-1 and enol-2) of CHD (Fig. 1), predicted by B3LYP/6-311++G(d,p), MP2/6-311++G(d,p) and MP2/cc-pVTZ theoretical methods are presented in Table 1. At all levels of calculation, the H-bonded enol tautomer (enol-1) is predicted to be the most preferred species, although the relative energies of the two enol tautomers over the diketo depend significantly on the method of calculation employed. Thus, according to B3LYP/6-311++G(d,p) and MP2/cc-pVTZ methods, the H-bonded enol tautomer (enol-1) is stable over diketo by ~19.0 kJ/mol, and we show below that this prediction is consistent with the experimental estimates from relative intensities of IR bands of the two species. On the other hand, MP2/6-311++G(d,p) method predicts that the energy difference between the two species is only ~7.6 kJ/mol. It is worth mentioning that such dissimilarity of the predicted relative energies of the tautomers for calculations by B3LYP/6-311G(d,p) and MP2/6-311G(d,p) methods was noted earlier by Shen et al. [7].

3.2. FTIR spectrum in N_2 matrix

The FTIR spectrum of CHD embedded in a solid N_2 matrix at 8 K temperature is shown in Fig. 2. The calculated infrared spectra of the most stable H-bonded enol-1 as well as diketo tautomers are presented in the lower panels. The relative intensities and assignments of the observed bands and calculated infrared intensities of the fundamentals of enol-1 tautomer are presented in Table 2. For further corroboration of the assignments, the observed and calculated spectral shifts of each band on deuteration of the enolic OH

Table 1
Relative energies, enthalpies, free energies and population of diketo and enol-1 tautomers calculated by DFT and MP2 methods.

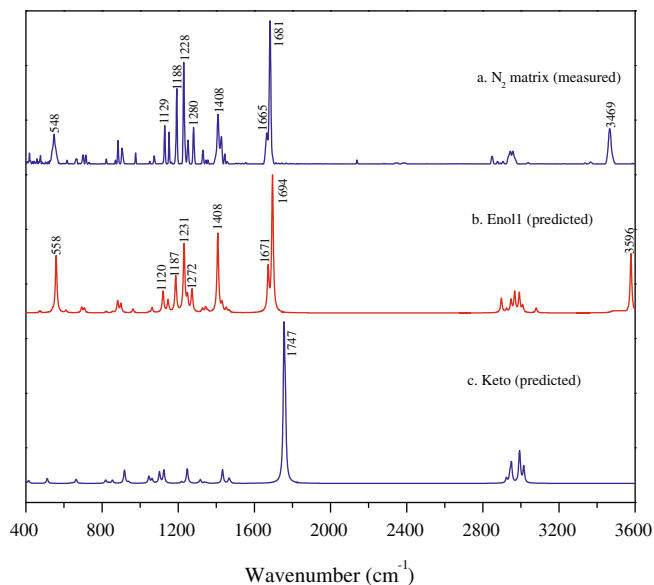| Thermodynamic parameters	B3LYP/6-311++G(d,p)		MP2/6-311++G(d,p)		MP2/cc-pVTZ	
	Enol-1	Diketo	Enol-1	Diketo	Enol-1	Diketo
ΔE (kJ/mol)	−19.2	0	−7.6	0	−19.0	0
$\Delta H°$ (kJ/mol)	−15.2	0	−5.0	0	−17.6	0
$\Delta G°$ (kJ/mol)	−11.9	0	−2.3	0	−14.2	0
Population from $\Delta G°$	99.2%	0.8%	71.9%	28.1%	99.7%	0.3%

Fig. 2. The FTIR spectrum of CHD in a N_2 matrix (a) and calculated spectra of enol-1(b) and diketo (c) tautomers at B3LYP/6-311++G(d,p) level.

$(\nu_{C=O} + \nu_{C=C})_{OOP} + \delta_{O-H}$

$\nu = 1695$ cm^{-1}

$(\nu_{C=O} + \nu_{C=C})_{IP} + \delta_{O-H}$
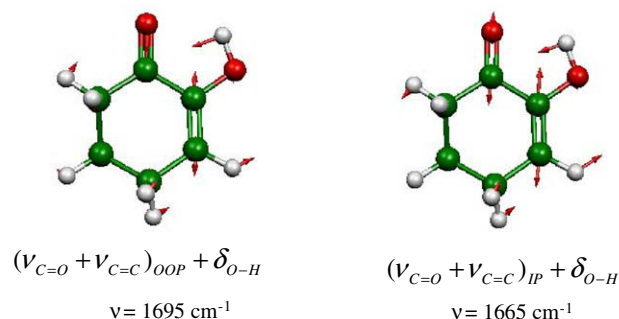
$\nu = 1665$ cm^{-1}

Fig. 3. Atom displacement vectors of two closely-spaced normal modes of enol-1 tautomer involving C=O stretching.

group (Fig. 4, shown below) are presented in the last two columns of Table 2. Thus, the band at 3469 cm^{-1} is assigned to the fundamental of O—H stretching vibration (ν_{O-H}) of the enol-1 tautomer, and it shows the largest deuterium isotope shift (see below). The obvious red-shifting of this band compared to the typical ν_{O-H} value of a free O—H group is a clear indication of intramolecular hydrogen bonding in the probed tautomeric species. The predicted
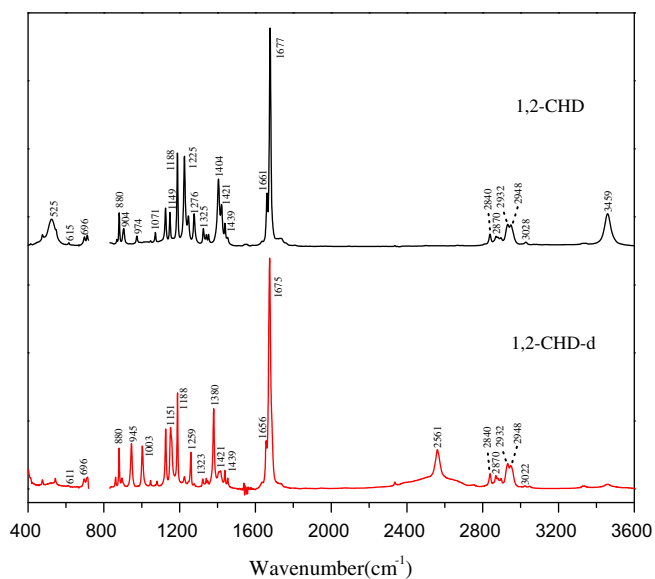
Table 2
Assignments of the vibrational bands in the FTIR spectrum of CHD in a cold N_2 matrix.

N_2 matrix		Calculated frequencies						Assignment	Mono deuteration shifts of CHD predicted by anharmonic calculation (cm^{-1})	Observed deuteration shifts of CHD in CCl$_4$ solution (cm^{-1})
		B3LYP/6-311++G(d,p) {Scaling−0.98}		MP2/cc-pVTZ {Scaling−0.975}		Anharmonic calculation at B3LYP/6-311++G(d,p) level				
Freq.	Int. (Rel.)	Freq.	Int. (Rel.)	Freq.	Int. (Rel.)					
3469	25	3596	43.5	3573	93	3459		ν_{O-H}	898	900
3036	0.9	3098	3.5	3128	4.6	3039		ν_{C-H} (enolic C—H)	10	6
2958	8.8	3027	5.1	3071	6.3	2943		ν_{C-H}	1	0
2944	8.8	3009	14	3059	19.9	2926		ν_{C-H}	0	0
2904	1.7	2985	14.9	3035	18.9	2911		ν_{C-H}	0	0
—	—	2966	9.1	3002	16	2928		ν_{C-H}	—	—
2876	1.7	2941	2.7	2983	4.4	2870		ν_{C-H}	0	0
2848	5.4	2914	10.5	2963	18.8	2813		ν_{C-H}	0	0
1681	100	1694	100	1681	100	1695		$(\nu_{C=O} + \nu_{C=C})_{O.P.} + \delta_{O-H}$	1	2
1665	22	1671	31	1667	45.5	1665		$(\nu_{C=O} + \nu_{C=C})_{I.P.} + \delta_{O-H}$	8	5
1458	1.5	1467	1.5	1464	1.8	1459		CH$_2$ sci.	2	0
1444	7.1	1452	4.7	1452	7.2	1438		CH$_2$ sci.	0	0
1427	19.3	1430	9.1	1430	49.4	1423		CH$_2$ sci.	0	0
1408	34.8	1408	57	1422	72.8	1395		$\nu_{C-O} + \delta_{O-H} + \delta_{C-H} + \nu_{C-C}$	39	26
1355	2.8	1355	2.7	1351	9.1	1353		$\delta_{C-H} + \delta_{O-H}$	3	4
1345	2.6	1344	4.8	1339	4.8	1337		$\delta_{C-H} + \omega_{CH_2}$	0	0
1329	9.6	1327	4.0	1328	15.2	1319		$\rho_{CH_2} + \delta_{C-H} +$ CH$_2$ twist	1	2
1280	25.5	1272	18.0	1282	25.3	1267		$\delta_{O-H} + \nu_{C-C} + \omega_{CH_2}$	13	17
1251	16.7	1249	15.1	1250	31.8	1247		$\delta_{O-H} + \delta_{C-O} +$ CH$_2$ twist	6	3
1228	71.2	1231	50.4	1228	99.6	1231		$\delta_{O-H} + \delta_{C-H}$	233	222
1188	51.9	1187	27.3	1196	44.3	1185		$\delta_{C-C} + \nu_{C-O} +$ CH$_2$ twist	0	0
1152	22.4	1147	10.0	1151	12.6	1145		$\nu_{C-O} +$ CH$_2$ twist $+ \delta_{C-H}$	1	2
1129	26.9	1120	16.0	1123	14.3	1118		CH$_2$ twist $+ \nu_{C-O} + \delta_{C-H}$	0	0
1073	5.6	1063	4.1	1070	5.3	1062		$\nu_{C-C} + \delta_{O-H}$	−12	−9
1050	1.8	1047	1.1	1044	1.5	1044		ρ_{CH_2}	0	0
976	7.6	962	3.0	975	5.4	964		$\nu_{C-C} + \delta_{O-H}$	22	28
904	11.1	899	7.1	899	13.2	902		$\gamma_{C-H} + \nu_{C-O}$	7	9
884	16.4	882	9.2	873	11.4	884		$\gamma_{C-H} + \rho_{CH_2}$	0	0
869	2.0	856	1.3	870	3.3	857		$\nu_{C-C} + \delta_{O-H}$	3	6
822	3.4	821	1.4	815	4.7	826		$\gamma_{C-H} + \rho_{CH_2}$	—	—
715	6.1	708	3.9	710	5.8	710		$\nu_{C-C} +$ ringdef.(O.P.) $+ \rho_{CH_2}$	0	0
701	6.3	693	4.0	698	6.3	694		Ringbreathing	0	0
616	2.0	611	2.1	610	8.0	616		$\rho_{CH_2} + \gamma_{O-H}$	4	4
548	20.8	558	41.7	588	66.1	555		γ_{O-H}	141	125
475	4.0	473	1.7	466	2.5	477		Ringdef.	0	0
—	—	411	0.2	403	0.8	414		Ringdef. (I.P.)	0	—
—	—	357	0.7	356	1.5	359		Ringdef. (O.P.)	5	—
—	—	322	8.0	321	15	319		H—bondstretching	11	—

ν, stretching; δ, inplane bending; γ, out of plane bending; ρ, rocking; ω, wagging.

Fig. 4. A comparison between the FTIR spectra of CHD (a) and mono-deuterated CHD (—OD) (b) in CCl$_4$ solution at room temperature.

Fig. 5. ^{1}H NMR spectrum of CHD in a CDCl$_3$ solution recorded using a 300 MHz machine at room temperature.

harmonic frequencies for this vibrational mode of CHD by B3LYP/6-311++G(d,p) and MP2/cc-pVTZ methods are 3596 and 3573 cm^{-1}, respectively. The large discrepancies between the measured and predicted frequencies, in spite of use of scale factors are indications of large anharmonic character of the mode. Furthermore, use of a uniform scale factor for the whole spectrum is found to be ineffective to correlate properly the predicted frequencies with the measured ones. On the other hand, the predicted anharmonic frequency of ν_{O-H} is 3459 cm^{-1}, and obviously it agrees much satisfactorily with the measured frequency. A comparison between the harmonic and anharmonic frequencies for other vibrational fundamentals is also presented in Table 2.

The carbonyl stretching fundamental ($\nu_{C=O}$) band of the probed tautomeric species appears doublet, where the higher frequency component at 1681 cm^{-1} is nearly five times more intense than the other component at 1665 cm^{-1}. Very similar feature is also seen in the calculated IR spectrum for the enol-1 tautomer (Fig. 2b). Visualization of the atom displacement vectors shows that both modes corresponding to this doublet involve stretching of C=O and C=C as well as bending of enolic OH group which is H-bonded with the adjacent carbonyl group (Fig. 3). In case of diketo tautomer, the predicted frequency for the symmetric C=O stretching fundamental (IR active) is 1742 cm^{-1}, however the measured spectrum (Fig. 2a) shows only a very weak band at this frequency. Likewise, all the bands in the finger print region of the spectrum can be assigned in terms of fundamentals of various IR active vibrations of the enol-1 tautomer. Therefore we conclude that in the cold (8 K) inert gas matrix environment, the molecule exists primarily in enol-1 form, and the population of the diketo tautomer is very small.

3.3. FTIR spectrum in CCl$_4$ solution

The spectrum recorded for a 0.01 M solution of CHD in CCl$_4$ at room temperature is shown in Fig. 4 (top panel). The overall appearance of this spectrum is similar to Fig. 2a, although, some of the bands of the former are red shifted by a few wavenumbers, and also the band at the $\nu_{C=O}$ absorption position of the diketo tautomer appears more prominent. The FTIR spectrum of the mono-deuterated isotopomer of CHD is displayed in the lower panel. A comparison between the two spectra shows clearly that the OH
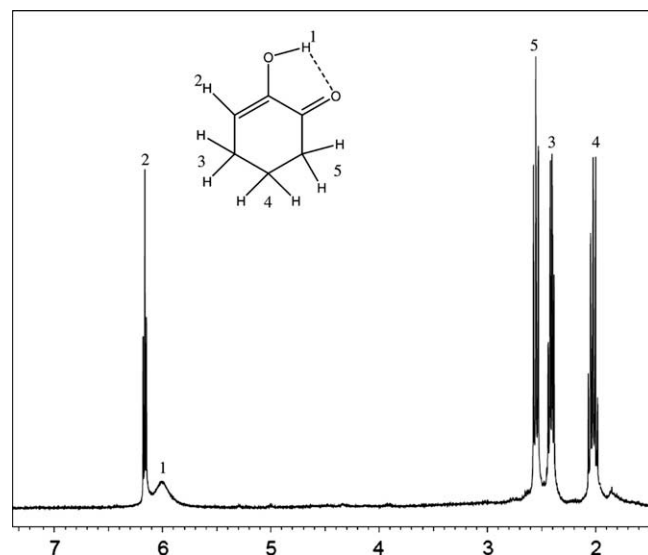
stretching fundamental at 3459 cm^{-1} in the top panel is shifted to 2561 cm^{-1} in the lower panel, and this is consistent with the predicted anharmonic frequency, 2559 cm^{-1}, for OD stretching of the deuterated enol-1 tautomer. Deuteration also causes some shifts for the two $\nu_{C=O}$ bands and those in the fingerprint region depending upon the nature of involvement of OH group in those modes. Thus, the bands at 1404, 1225, 974 and 525 cm^{-1} exhibit a relatively larger shifts, whereas those at 3028, 1661, 1276, 1071 cm^{-1}, etc. experience relatively smaller shifts, and rest of the bands show no shift at all. The observed shifts of different modes along with those predicted by calculation at B3LYP/6-311++G(d,p) level are presented in Table 2.

The ^{1}H NMR spectrum of CHD recorded in CDCl$_3$ solution at room temperature is presented in Fig. 5, and obviously the spectral features are consistent with enol-1 tautomer. The broad peak at 6 ppm represents the chemical shift of the H-bonded OH proton. The sharp triplet band near 6.2 ppm can be associated with the enolic CH proton, and the corresponding predicted chemical shifts by B3LYP/6-311++G(d,p) method for the enol-1 tautomer are 5.9 and 6.2 ppm, respectively. The other peaks in the spectrum appear in the range of 2–3 ppm.

3.4. FTIR spectrum of CHD vapour

The spectrum of CHD vapour recorded using a low-pressure multi-pass gas cell at room temperature is shown in Fig. 6. The effective path length of the gas cell is 8 m. The ν_{O-H} band of the enol-1 tautomer appears at 3484 cm^{-1} with a matrix to gas shift of +15 cm^{-1}. A weak vibrational feature in the vicinity (3369 cm^{-1}) is assigned to first overtone of $\nu_{C=O}$, and the corresponding predicted frequency by anharmonic calculation is 3376 cm^{-1}. The doublet feature of the C=O stretching fundamental is not resolved here because of overlap between the rotational contours of the two bands. The maximum of the overlapped feature appears at 1694 cm^{-1}, and it is blue-shifted by 13 cm^{-1} from the more intense doublet component of the matrix spectrum.

A comparison of the gas-phase spectrum with those in Figs. 2a and 4 reveals that the weak band at 1744 cm^{-1}, which match nicely with the predicted frequency of the symmetric C=O stretching fundamental of the diketo tautomer (Fig. 2c), appears more distinct. Therefore, the band could be an indication for the presence of a small fraction of diketo population in the gas phase and this
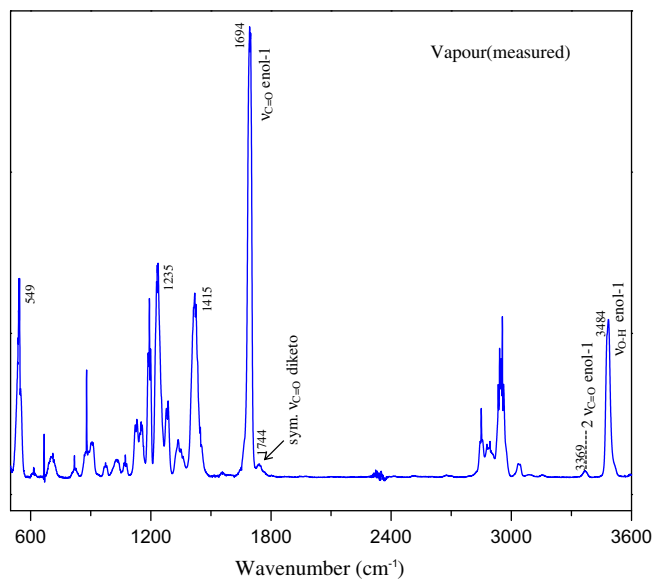
Fig. 6. The FTIR spectrum of CHD vapour ($\sim 10^{-3}$ mbar) at room temperature in a multi-pass gas cell.

is consistent with the conclusion of Shen et al. following an electron diffraction study of CHD in the gas phase [7]. As pointed out above, the intensity of this band is much weaker in the cold matrix spectrum indicating that the population of the diketo tautomer is relatively smaller in the matrix. Although a higher energy isomeric species, populated in the gas phase at room temperature, is expected to be trapped in a low temperature matrix, the features of our measured spectra indicates a kind of relaxation of the diketo tautomer to the most favoured enol-1 form as a result of soft collision with the solid matrix surface [9]. Such phenomenon of collisional relaxation of a higher to lower energy isomeric forms is quite common in collisional cooling of supersonic jet expansion [10,11]. An alternative assignment as overtone or combination tone of lower frequency modes of enol-1 tautomer is also not pos-

sible because of its smaller intensity in the matrix. Further discussion on this point is presented in the following section.

In Fig. 7, we have shown the changes of $\nu_{C=O}$ and ν_{O-H} band intensities of enol-1 tautomer for increasing the temperature of the gas cell from 25 to 65 °C. At a higher temperature, the intensity of these two bands is lowered to a little extent. Although a general reason for lowering of the peak height of a band at a higher temperature could be due to redistribution of rotational population, which usually causes broadening of the band widths, however, no distinct broadening is noted in the present case. Therefore, the peak height lowering could be an indication of redistribution of the tautomeric population. A simple population analysis using the calculated ΔG value shows that for the said temperature increase, the population of enol-1 tautomer could be lowered from 99.2% to 98.4%. Taking into consideration of the peak areas of the 1694 and 1744 cm^{-1} bands, the relative population of the tautomer (enol-1) at the two said temperatures is estimated to be 98.5% and 98.1%, respectively, which are quite consistent with the expectation. The same experiment was also performed on a CCl$_4$ solution of CHD and the results are presented in the inset of Fig. 7. In the solution phase the doublet of the $\nu_{C=O}$ band appears prominent, and the intensity of both the components decreases with increase in temperature and this confirms that both bands belong to the same tautomeric species. However the intensity of the weak feature (at 1742 cm^{-1}) assigned to symmetric $\nu_{C=O}$ of the diketo tautomer shows a slight enhancement with temperature.

3.5. FTIR spectrum of the neat sample

The FTIR spectrum of the neat sample of CHD is shown in Fig. 8. The spectrum was recorded at room temperature using the attenuated total reflection (ATR) mode of a commercial infrared spectrometer (Bruker Optics, model: Alpha). An instrument resolution of 4.0 cm^{-1} was used for this measurement, and each spectrum was averaged over 256 scans. The key feature of the spectrum is larger intensity of the 1736 cm^{-1} band, which we assign to sym-
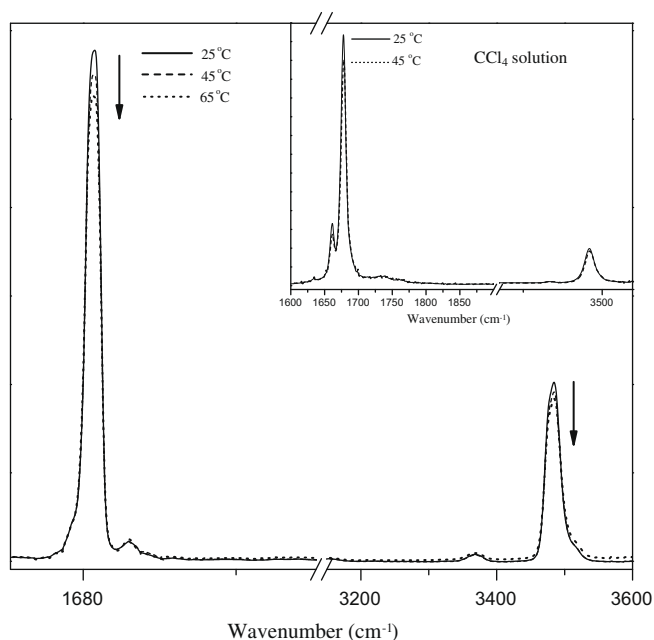

Fig. 7. The effect of temperature variation on intensities of $\nu_{C=O}$ and ν_{O-H} bands of CHD in vapour and in CCl$_4$ solution (inset).
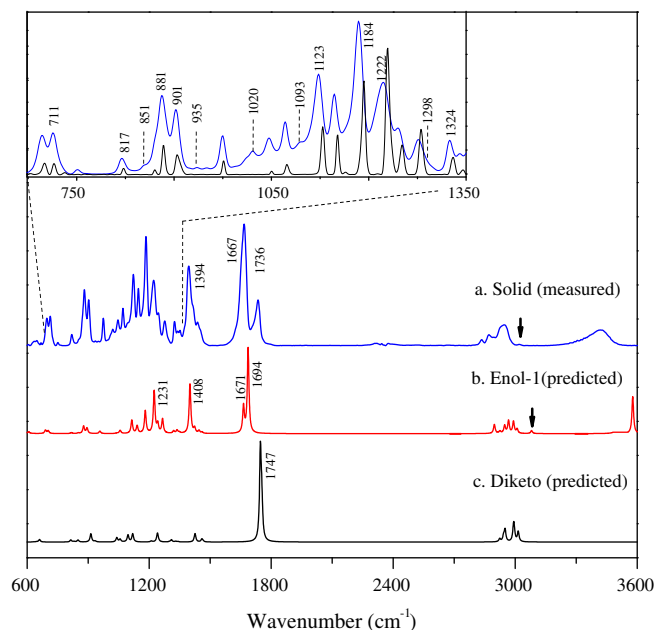

Fig. 8. The FTIR spectrum of neat CHD recorded using ATR mode (a) and calculated spectra of enol-1(b) and diketo (c) tautomers at B3LYP/6-311++G(d,p) level. The inset (topmost panel) shows a comparison, in a segment of the fingerprint region, between the neat solid spectrum and the matrix spectrum. The bands due to diketo tautomer are indicated by vertical lines in the spectrum.

Table 3
Medium effect on a few selected bands of CHD and the predicted anharmonic frequencies of the corresponding modes.

IR frequency (cm^{-1})			Anharmonic calculation B3LYP/6-311++G(d,p)	Assignment
N$_2$ matrix	Gas phase	Neat sample		
3469	3484	3427	3459	ν_{O-H}
3036	3040	3022	3039	ν_{C-H} (enolic C—H)
—	1744	1736	1742 (diketo)	$\nu_{C=O}^{sym.}$
1681	1694	1667	1695	$(\nu_{C=O} + \nu_{C=C})_{O.P.} + \delta_{O-H}$
1665	—	—	1665	$(\nu_{C=O} + \nu_{C=C})_{I.P.} + \delta_{O-H}$
1355	1360	1352	1353	$\delta_{C-H} + \delta_{O-H}$
1345	1349	1341	1337	$\delta_{C-H} + \omega_{CH_2}$
—	—	1298	1305 (diketo)	$\delta_{C-H} + \nu_{C-C}$
1280	1286	1277	1267	$\delta_{O-H} + \nu_{C-C} + \omega_{CH_2}$
1228	1235	1222	1231	$\delta_{O-H} + \delta_{C-H}$
1129	1130	1123	1118	CH_2twist $+ \nu_{C-O} + \delta_{C-H}$
—	—	1093	1101 (diketo)	$\delta_{C-H} + \nu_{C-C}$
—	—	1020	1049 (diketo)	CH_2twist
—	—	950		
—	—	935	939 (diketo)	ν_{C-C}
884	880	881	884	$\gamma_{C-H} + \rho_{CH_2}$
—	—	851	857 (diketo)	ρ_{CH_2}
548	549	—	555	γ_{O-H}

metric $\nu_{C=O}$ of the diketo tautomer. As shown in Table 3, the predicted gas phase anharmonic frequency for the fundamental is 1742 cm^{-1}, and in the spectrum of CHD vapour the band appears weakly at 1744 cm^{-1}. The relatively large intensity of this band in the neat sample in comparison to $\nu_{C=O}$ of the enol-1 tautomer, which is red shifted here to 1667 cm^{-1}, indicates that the diketo tautomer is more stabilized in the neat sample. The origin of this excess stability can be understood in the following way. The electronic structure calculation predicts that the dipole moment of the diketo tautomer (5.61 D) is much larger compared to the enol-1 (3.6 D). Therefore, the intermolecular electrostatic interactions stabilize the former in the neat solid, although under isolated condition it is less favoured compared to enol-1 form. This conclusion is somewhat consistent with the suggestion of Walzl et al. that CHD exists exclusively in the ketonic form in the solid phase [12]. The same interactions are also responsible for larger band-widths and congestion in the fingerprint region of the spectrum (Fig. 8). The bottom panel shows that the predicted intensities of the bands in the fingerprint region of the diketo tautomer are much weaker. For better visualization of the bands corresponding to this tautomer, the fingerprint region of the pure solid spectrum is compared with the matrix-isolation spectrum in the inset (on the top of the trace a). It shows clearly that the bands at 851, 935, 1020, 1093 and 1298 cm^{-1} in the former spectrum (indicated by vertical dotted lines) are absent in the latter, and all of them are corresponded with the diketo tautomer, which display very good agreement with the predicted IR fundamentals considering the fact that in pure solid the IR frequencies in this spectral region display 8–12 cm^{-1} red-shifting compared to their positions in a gas-phase spectrum. The

medium dependence of a few selected intense bands, their assignments and their predicted anharmonic frequencies by B3LYP/6-311++G(d,p) method are presented in Table 3.

4. Summary and conclusion

Keto–enol equilibrium of 1,2-cyclohexanedione has been probed by use of FTIR spectroscopy in the neat sample, CCl$_4$ solution, vapour phase and by embedding the molecules in a cold nitrogen matrix. The equilibrium is found to be influenced greatly by the medium and thereby the intermolecular interactions. In a cold N$_2$ matrix, only the intramolecularly H-bonded enol-1 tautomer is identified. On the other hand, the spectrum of the neat solid sample at room temperature shows signatures of large diketo tautomer population. The symmetric carbonyl stretching fundamental of this tautomer weakly appears in the FTIR spectra of the vapour and in CCl$_4$ solution at room temperature. Larger dipole moment of the diketo tautomer compared to the enol-1 is assumed to be responsible for larger stability of the former in neat solid. The relative energies of different tautomers predicted by B3LYP/6-311++G(d,p) and MP2/cc-pVTZ methods are consistent with the observations. However, the MP2/6-311G(d,p) and MP2/6-311++G(d,p) methods overestimate the stability of the diketo tautomer. Complete assignment of the mid-IR spectrum of CHD in the cold N$_2$ matrix has been suggested with the aid of the spectra predicted by theoretical methods. The predicted vibrational fundamentals by anharmonic calculations at B3LYP/6-311++G(d,p) level and measurements of deuterium isotope shifts of the bands were immensely useful for unambiguous assignment of ν_{O-H} and other bands of the tautomers.

References

[1] S.M. Kupchan, R.W. Britton, J.A. Lacadie, M.F. Ziegler, C.W. Sigel, J. Org. Chem. 40 (1975) 648.
[2] N. Fukamiya, K. Lee, I. Muhammad, C. Murakami, M. Okano, I. Harvey, J. Pelletier, Cancer Lett. 220 (2005) 37.
[3] (a) K. Hoffken, W. Jonat, K. Possinger, M. Kolbel, T.H. Kunz, H. Wagner, R. Becher, R. Callies, P. Friederich, W. Willmanns, H. Maass, C.G. Schmidt, J. Clin. Oncol. 8 (1990) 875;
(b) T. Pickles, L. Perry, P. Murray, P. Plowman, Br. J. Cancer 62 (1990) 309.
[4] M.A. Gianturco, A.S. Giammarino, R.G. Pitcher, Tetrahedron 19 (1963) 2051.
[5] J.T. Francis, A.P. Hitchcock, J. Phys. Chem. 98 (1994) 3650.
[6] G. Bouchoux, Y. Hoppilliard, R. Houriet, New J. Chem. 11 (1987) 225.
[7] Q. Shen, M. Traetteberg, S. Samdal, J. Mol. Struct. 923 (2009) 94.
[8] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian 03, Revision E.01, Gaussian, Inc., Pittsburgh, PA, 2003.
[9] P. Huber-walchli, Hs.H. Günthard, Spectrochim. Acta A 37 (1981) 285.
[10] R.S. Rouff, T.D. Klots, H.S. Gutowsky, J. Chem. Phys. 93 (1990) 3142.
[11] S.S. Panja, T. Chakraborty, J. Chem. Phys. 118 (2003) 6200.
[12] K.N. Walzl, I.M. Xavier Jr, A. Kuppermann, J. Chem. Phys. 86 (1987) 6701.