Spectroscopic study of overtone and combination bands in aliphatic aldehydes

Y. Dwivedi, S.B. Rai *

Laser and Spectroscopy Laboratory, Department of Physics, Banaras Hindu University, Varanasi, U.P. 221005, India

ABSTRACT

Overtone spectra of C–H stretching vibrations of formaldehyde, acetaldehyde and n-butyraldehyde have been studied in liquid phase using conventional absorption and thermal lens techniques. The overtone bands up to $\Delta v = 4$ have been monitored using the conventional IR and NIR techniques and the band involving $\Delta v = 7$ of the C–H stretching vibration with thermal lens technique. The vibrational frequencies and the anharmonicity constants for C–H stretching vibrations of the methyl as well as of the aldehyde groups for all the three molecules have been determined using these data. We have also calculated the vibrational frequencies of fundamental bands and charge distribution on carbon and hydrogen atoms using ab initio methods and the results are compared with the experimental data.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Spectroscopic studies of molecules in their highly excited vibrational levels in ground electronic state provide valuable information on radiative transitions, photo-dissociation of molecules and the chemical reactivity of the concerned bond [1]. The local mode model has been widely used for the interpretation of the overtone bands involving higher vibrational quantum numbers [2,3]. This model treats a molecule as a set of loosely coupled anharmonic oscillators (localized on the individual C–H bonds) and has been successfully employed to explain the appearance of the overtone absorption bands in a number of polyatomic molecules, including aliphatic, aromatic and halo-methanes [4–6]. It includes anharmonic potential function for the highly excited C–H oscillators by using an internal co-ordinate system localized on the chemical bonds. Earlier studies on the overtone spectra of polyatomic molecules were limited to bands involving low vibrational quantum numbers but with the advent of sensitive techniques such as long path absorption by multiple reflections, putting the sample cell in laser cavity, photo-thermal and photoacoustic spectroscopy, precise measurements of very weak overtone bands are possible [7]. Extensive work has been carried out on the vibrational spectroscopy of formaldehyde and its deuterated compounds in all the three phases. Salant and West [8]

observed a large number of bands in formaldehyde, in the 8000–4590 cm^{-1} region, and assigned them as overtone and combination bands. Though the assignments of various fundamentals are fairly unambiguous, there is some confusion as regards the bending vibrations and combination bands. Perrin et al. [[9] and references therein] reported a comprehensive list of the lines/bands in formaldehyde in the spectral region 3200–2400 cm^{-1}.

The vibrational spectrum of acetaldehyde and deuterated acetaldehyde have also been studied by a large number of workers [10–22]. The early investigation by McKean [[10] and references therein] on nearly fully deuterated gas phase acetaldehyde molecule, showed that the two bands at 2815 and 2718 cm^{-1} (in gas phase) form a Fermi resonance dyad involving the aldehyde C–H stretching ($v_{C–H}$) and two quanta of $\delta_{C–H}$. He also assigned the higher energy band (3002 cm^{-1}) as in-plane and the lower energy band (2944.5 cm^{-1}) as out-of-plane C–H stretching of $v_{as}(CH_3)$. McKean [11] has also reported that a C–H bond trans to another C–H bond has a lower vibrational frequency than a C–H bond trans to the methyl group. Nakagaki and Hanazaki [12] in a later study concluded that the higher energy band is due to the out-of-plane and the lower energy band to in-plane C–H stretching of $v_{as}(CH_3)$, on the basis of intensity measurements, which were also supported by electron diffraction and microwave studies, reported by Harmony et al. [13] and Pitzer and Weltner [14]. Fang et al. [15] recorded the C–H overtone spectra of the aldehyde group in acetaldehyde. They observed that the absorption strength of the higher C–H overtone bands of aldehyde group are 3–5 times larger than for the C–H of methyl group. This is in contrast to the intensity

* Corresponding author. Tel.: +91 542 2307308; fax: +91 542 2369889.
  E-mail address: sbrai49@yahoo.co.in (S.B. Rai).

pattern observed for the fundamental and the first overtone band, where the strength of the aldehyde C–H absorption is quite low [16]. On the basis of these studies, Fang et al. [15] concluded that the aldehyde C–H bond has a relatively large (electrical) anharmonicity. Findsen et al. [17] reexamined the spectra of acetaldehyde, and assigned the higher frequency component as the in-plane and lower frequency component as the out-of plane C–H stretching of $\nu_{as}(CH_3)$, on the basis of the studies of the effect of electron and lone pair interactions using local mode model and the molecular orbital theory. Pople et al. [19] and Nosberger et al. [20] in their work supported the assignment of McKean [10,11]. Hanazaki et al. [21] in their later work also found the more intense in-plane C–H stretching of $\nu_{as}(CH_3)$ lie at higher energy in acetaldehyde, thus eliminating the uncertainty. The influence of electron lone-pair, situated on a hetero atom (oxygen atom of C=O), on the neighboring methyl group is explained in terms of donation of electron population from the lone-pair into the antibonding orbital associated with the C–H bond oriented trans to the lone-pair. To the best of our knowledge overtone bands in n-butyraldehyde are not reported in the literature.

In the present work we have studied the overtone spectra of C–H stretch vibrations of formaldehyde, acetaldehyde and n-butyraldehyde in liquid phase using conventional absorption and thermal lens techniques and assigned different overtone and combination bands arising in this region of spectrum. The local mode model has been used to determine the vibrational frequencies and the anharmonicity constants for the C–H stretching vibrations of the methyl as well as of the aldehyde groups.

2. Experimental

The samples of formaldehyde, acetaldehyde and n-butyralde-hyde were obtained from Riedel with a purity of 99.9%. These samples were doubly distilled and filtered with Glaxo 5 μm filter paper before use for recording the spectra. The IR spectra of these compounds were recorded using a PerkinElmer double beam IR spectrophotometer (Model 883) whereas for the NIR spectra a Cary 2390 (Varian Associates) double beam spectrophotometer was used. For all the measurements 10-mm quartz sample cells were used. For dual beam thermal lens measurements a cw Ar$^+$ pumped tunable ring dye laser (570–610 nm) with a 400 mW power at ~600 nm were used as pump source and a 2 mW He–Ne laser was used as a probe source. For wavelength calibrations, optogalvanic signal of Ne was recorded simultaneously passing one part of the beam in a Fe–Ne hollow cathode lamp [22,23].

3. Results and discussion

Geometries of the three aldehyde derivatives were interrogated by the evaluation of their harmonic vibrational frequencies and charge distribution by three different theories viz. restricted Hartree–Fock (RHF), density functional theory (DFT) using Becke's three parameter hybrid exchange function with the LYP (Lee, Yang
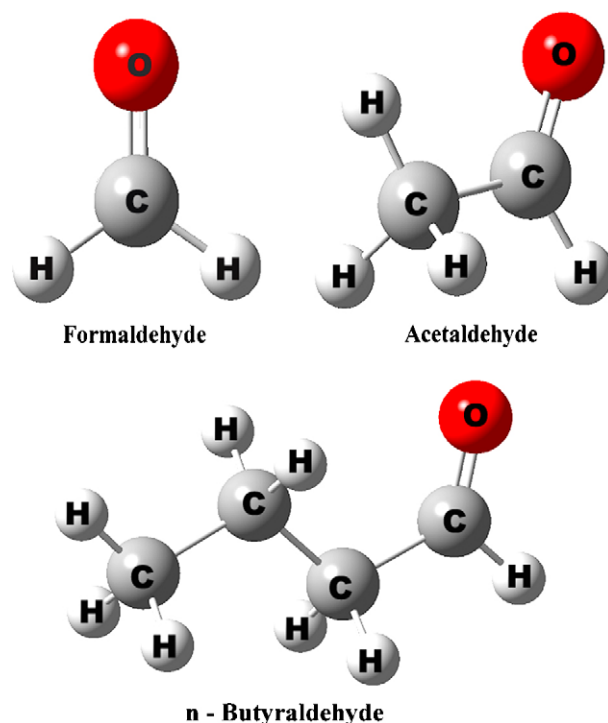

Fig. 1. Optimized geometries and atomic labels for aliphatic aldehyde derivatives.

and Parr) correlation function and second-order Møller-Plesset (MP2) methods using standard 6-311G* basis set. The calculations have been carried out using *GAUSSIAN* 98 program suite [24]. The geometries of the three molecules are displayed in Fig. 1 and the bond lengths and bond angle values, related to them are collected in Table 1. It is noteworthy that the geometries obtained from the three methods are similar with a slight variation in bond lengths and bond angles. In particular RHF method gives the shortest bond lengths while MP2 predict the longest bond length. Also the charge density on the 'O' atom and the attached 'C' atom, are found to increase, from formaldehyde to butyraldehyde, in all the methods. Our optimized geometry is in good agreement with the geometry reported by Hanazaki et al. [21] by SCFMO scheme using 6-31G** basis set.

The absorption spectra of n-butyraldehyde molecule in the spectral region of 12,500–5000 cm^{-1} is shown in Fig. 2. The IR spectra of all the three molecules show a large number of characteristic bands in the fingerprint region 4000–200 cm^{-1}. Broad bands at 1740, 1720 and 1735 cm^{-1} are observed for formaldehyde, acetaldehyde and butyraldehyde, respectively, due to C=O stretching vibration. All the three molecules show two bands in the region 2840–2720 cm^{-1} which are Fermi resonance dyads arising from the mixing of the fundamental C–H stretch and two quanta of the deformation bands [25,10]. Though both bands have a mixed character, the peak lying at 2790 cm^{-1} in

Table 1
Optimized geometry parameters of the aldehyde molecules.

Theoretical method used	Formaldehyde				Acetaldehyde					n-Butyraldehyde				
	Bond length		Charge on O atom	Angle ∠HCO	Bond length			Charge on O atom	Angle ∠HCO	Bond length			Charge on O atom	Angle ∠HCO
	–CH$_2$	C=O			–CHO	–CH$_3$	C=O			–CHO	–CH$_3$	C=O		
RHF	1.094	1.178	0.345	122.0	1.097	1.086	1.182	0.377	120.0	1.098	1.085	1.182	0.383	119.9
DFT	1.110	1.200	0.251	122.6	1.114	1.096	1.203	0.274	120.2	1.114	1.090	1.205	0.279	120.1
MP2	1.100	1.212	0.358	121.9	1.110	1.094	1.214	0.391	120.1	1.111	1.090	1.215	0.397	120.0