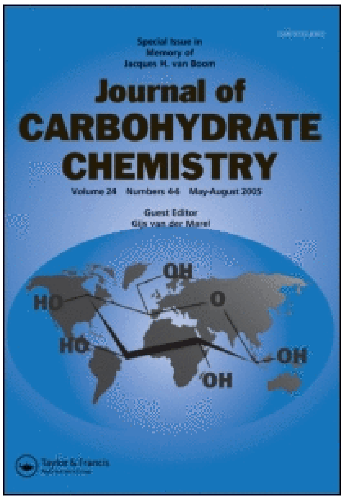

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β-Cyclodextrin Complexes of Benzaldehyde, Vanillin and Cinnamaldehyde: A Raman Spectroscopic Study[1]

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β-CYCLODEXTRIN COMPLEXES OF BENZALDEHYDE, VANILLIN AND CINNAMALDEHYDE: A RAMAN SPECTROSCOPIC STUDY [1]

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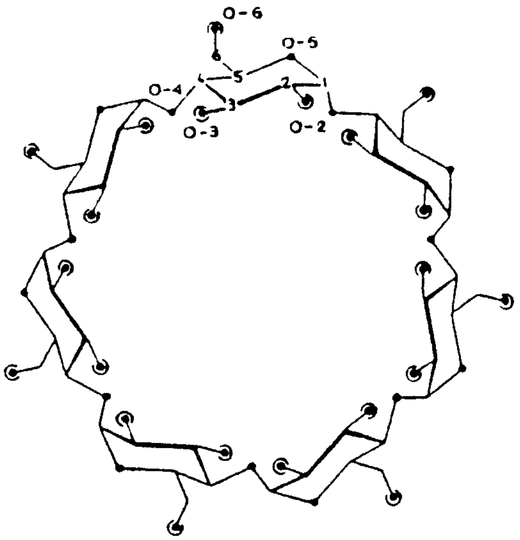
ABSTRACT

Raman spectra of benzaldehyde, vanillin and *trans*-cinnamaldehyde, and of their complexes in β-cyclodextrin are presented and discussed. The guest molecules provide both an aromatic ring for privileged interaction with the cyclodextrin cavity, and characteristic vibrations (*e.g.*, νC=O, νC=C, νCC_ϕ (ϕ=phenyl), $\nu C\text{-}H_\phi$) with group frequencies in spectral regions free from cyclodextrin bands which are useful for probing the guest perturbed by complex formation with β-cyclodextrin. In particular, the C=O bond is shown to be a good vibrational spectroscopic probe to monitor the effects of both the medium, through its dielectric constant, and of specific interactions, namely of the hydrogen bonding type. The first of these effects is evaluated theoretically and a Kirkwood-Bauer-Magat plot for benzaldehyde is used to estimate the effective dielectric constant for the guest in the benzaldehyde-β-cyclodextrin complex. The above mentioned Raman spectroscopic results are interpreted and discussed.

INTRODUCTION

Cyclodextrins (CD's) are cyclic oligosaccharides consisting of six, seven and eight α(1-4)-linked D-glucopyranose units, named αCD, βCD (Scheme 1) and γCD. They have the form of short truncated cones, with the wide and narrow rims occupied by the secondary



Scheme 1

and primary hydroxyl groups, respectively. The central cavities of these molecules are hydrophobic in nature and form inclusion complexes with a wide variety of molecules based on physical fit and chemical affinity. Due to the size and the dominant hydrophobic character of the cavity, the included molecular fragment is, quite often, an aromatic ring.

In this work, the Raman spectra of the different molecules — benzaldehyde (Bnz), *trans*-cinnamaldehyde (Cin) and vanillin (Van) — included in β-cyclodextrin (βCD) are presented and discussed. The guest molecules provide both an aromatic ring for favoured interaction with the CD cavity, and group frequencies, namely νC=O, νC=C, νCC_{ϕ}, and νCH_{ϕ}, for probing the guest by Raman spectroscopy. An *ab initio* self-consistent reaction field (SCRF) calculation with the 6-31G* basis set [2] was carried out for Bnz in media of different dielectric constants, and the C=O stretching frequency calculated. A Kirkwood-Bauer-Magat (KBM) plot [3] for Bnz is drawn and the calculated frequencies scaled so that the Raman C=O stretching frequency for a diluted solution of Bnz in CCl_4 falls in the same KBM linear relationship. In addition, this straight line is used to estimate the effective dielectric constant for Bnz in the Bnz-βCD complex. The C=O frequency shift due to specific interactions of the hydrogen bonding type is also estimated for this complex and the above mentioned Raman spectroscopic results are interpreted and discussed.

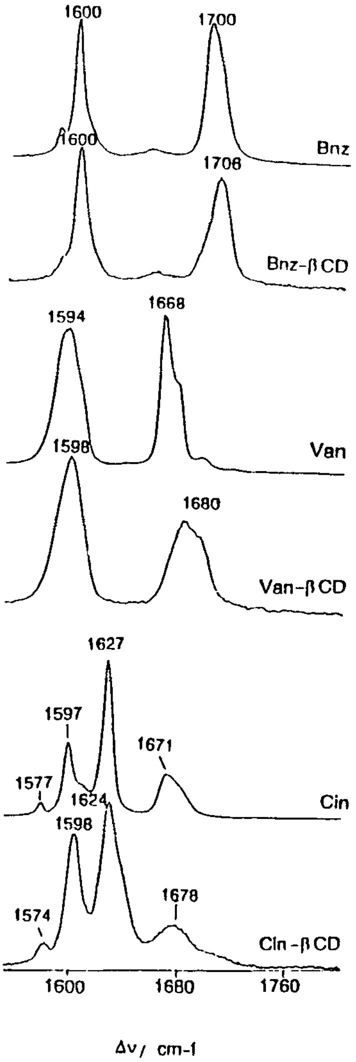


Figure 1. Raman spectra of X (X=Bnz, Van, Cin) in X-βCD compounds in the 1550-1800 cm^{-1} region.

RESULTS AND DISCUSSION

Figure 1 presents the Raman spectra of X and X-βCD compounds (X= Bnz, Van, Cin) in the 1550-1800 cm^{-1} region. The more relevant spectral features presented in these spectra are νCC_{ϕ} (*ca.* 1600 cm^{-1}), $\nu C{=}O$ (1668-1706 cm^{-1}) and, for X=Cin, $\nu C{=}C$(1624-1627 cm^{-1}).

Table 1. Raman frequencies (cm^{-1}) [a]

System	νC=C	νC=O	ΔνC=O	νC-H_{ar}	ΔνC-H_{ar}
Bnz		1700	—	3073	—
Bnz-βCD		1706	6	3064	-9
Van		1668	—	3074	—
Van-βCD		1680	12	3076	2
Cin	1627	1671	—	3065	—
Cin-βCD	1624	1678	7	3058	-7

a. For asymmetric band shapes, single quoted frequencies correspond to maxima of band envelopes.

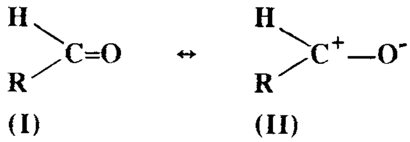
Table 1 summarizes the most important spectral results including νC-H_{ar} which occurs in a frequency region relatively free from other νC-H bands. It can be seen that positive and negative frequency shifts of νC=O and νC-H_{ar} are found for both Bnz and Cin, respectively, on inclusion in βCD. In turn, the largest increase of the C=O frequency occurs for Van-βCD, with a small increase observed for νC-H_{ar}.

Two types of spectral comparisons emerge both from the Raman spectra shown in Figure 1 and the frequency and intensity results presented in Table 1, namely,

i) between the pure guests,

ii) between X and X-βCD, for a particular guest X.

Comparison i) enables to assess substituent effects in the guest molecule and the extent of conjugation between the system of π electrons and the C=O bond. To this end, two canonical structures are particularly relevant, namely,



Scheme 2

In fact, the order of increasing frequencies for the carbonyl stretching frequency (Figure 1 and Table 1) is

$$\text{Van} < \text{Cin} < \text{Bnz}, \qquad (1)$$

in consonance with the decreasing order of the donor character of R, namely,

$$\text{R:} \qquad \phi'\text{-OH}_{para} > \text{CH=CH-}\phi > \phi \qquad (2)$$

where ϕ represents a phenyl radical and ϕ' stands for a 3-methoxyphenyl fragment. In fact, better electron donation by R causes an increased contribution of structure II (Scheme 2) which, in turn, leads to a lower carbonyl stretching frequency.

Considering now comparison ii), it should be pointed out that the inclusion process involves the following transformation,

$$\textbf{pure guest in condensed phase} \longrightarrow \textbf{guest in the } \beta\textbf{CD cavity.} \qquad (3)$$

This process leads to conclusions concerning solvent effects and specific interactions that affect νC=O. This kind of comparison reveals

a) frequency shifts of band maxima and

b) significant changes in asymmetric band envelopes.

While the latter effect b) implies overlapping of various component bands which in turn points to the occurrence of different and relatively specific environments for C=O, *i.e.*, to the existence of specific interactions, namely of the hydrogen bonding type, effect a) may result both from the occurrence of bulk solvent effects and of specific interactions. Hence, the overall frequency shift can be expressed as

$$\Delta\nu = \nu_0 - \nu = \Delta\nu_\varepsilon + \Delta\nu_{sp}, \qquad (4)$$

where ν_0 is the frequency for "vacuum" (ε=1), and $\Delta\nu_\varepsilon$ and $\Delta\nu_{sp}$ represent the shifts due to a medium with dielectric constant ε and to specific interactions, respectively.

The inclusions of Bnz, Van and Cin are accompanied by positive carbonyl frequency shifts, ΔνC=O (Figure 1 and Table 1), *i.e.*, by increasing of νC=O, thus suggesting a reduced contribution from canonical form II, *i.e.*, a greater contribution of structure I (Scheme 2). In addition, νC-H$_{ar}$ exhibits negative frequency shifts for Bnz and Cin, pointing to small, yet significant, decreases of electronic density in the ring C-H bonds, moving away from these bonds into the aldehydic C=O bond. For Van, the donor characters of both the methoxy and hydroxyl groups in *meta* and *para* positions, respectively, tend to compensate for that transfer of electronic density, thus producing a net small positive shift in νC-H$_{ar}$.

In order to estimate the effect of the medium on the carbonyl stretching frequency, *ab initio* MO calculations with the 6-31G* basis set and full optimization of the Bnz geometry were carried out, and the self-consistent reaction field (SCRF) method was

Table 2. Calculated carbonyl frequencies (cm^{-1}) of benzaldehyde in media of different dielectric constants

ε	νC=O [a]	νC=O [b]
1.0	2004	1719
6.0	1989	1706
17.4	1985	1703
80.0	1983	1701

a. Calculated non-scaled values. b. Calculated scaled values; the scaling factor (0.8578) reproduces the C=O stretching frequency observed for a diluted solution of Bnz in CCl_4 (1711 cm^{-1}).

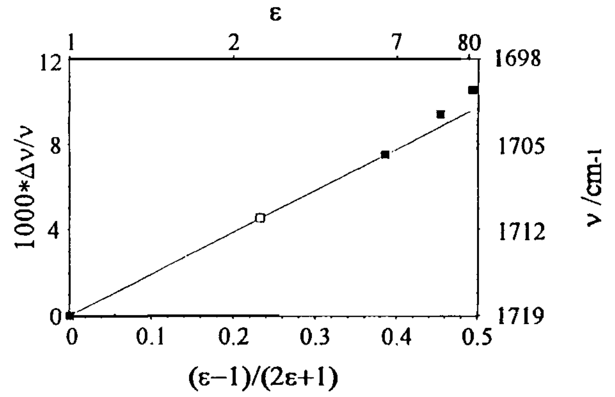


Figure 2. KBM plot for the calculated C=O stretching frequency (cm^{-1}) of Bnz in media of different dielectric constants. The open square corresponds to a 0.1 M solution of Bnz in CCl_4.

subsequently applied, assuming that the molecule was included in a medium of dielectric constant, ε. Different values of ε were considered and the calculated C=O stretching frequencies are presented in Table 2.

In order to scale these calculated frequencies properly, the Raman spectrum of a dilute solution of Bnz in CCl_4 (0.1 M) was recorded. Since no effect other than the medium effect is expected for such a solution and the dielectric constant of the solvent is sufficiently low, a linear KBM relationship should be obtained. Hence, the scaling factor for the above calculated frequencies (0.8578) was chosen so that the experimental value of νC=O for Bnz in CCl_4 (1711cm^{-1}; ε=2.24) would fall in a KBM straight line defined by the ε=1.0 and 6.0 points. This KBM linear relationship (Figure 2) has a slope of 19.44 and yielded the C=O Raman frequency for Bnz in "vacuum" (ε=1) equal to 1719 cm^{-1} (see Table 2).

The above mentioned KBM slope for Bnz is smaller than for formaldehyde (27.09),[3] *i.e.*, the same dielectric constant produces a smaller relative frequency shift $\Delta\nu/\nu$, consonant with the donor mesomeric effect of the aromatic ring in Bnz, leading to polarization of the C=O bond, thus increasing the contribution of form II (Scheme 2).

For a Bnz molecule included in a medium of ε=17.4 (the dielectric constant for pure Bnz), the SCRF calculation yields $\Delta\nu_\varepsilon \approx 16$ cm^{-1}, a value which is 1 cm^{-1} larger than the one evaluated using the above mentioned KBM linear relationship for Bnz (see Figure 2). Hence, from Expression 4, it can be estimated that $\Delta\nu_{sp}$ is *ca.* 3-4 cm^{-1} for liquid Bnz.

If it is assumed that this shift is also valid for the Bnz-βCD complex and the observed Raman frequency (1706 cm^{-1}, see Figure 1) is used, then $\Delta\nu_\varepsilon \approx$9-10 cm^{-1} for this inclusion complex. From this $\Delta\nu_\varepsilon$ value, the KBM relationship yields an effective dielectric constant for βCD *ca.* 3. Being too low, [5] this value suggests a predominantly hydrophobic environment. However, a word of caution should be said, since the last assumption, specific interactions producing the same carbonyl frequency shift for liquid Bnz and the Bnz-βCD complex, may be too drastic. In addition, for a Bnz molecule included in the βCD cavity, the medium is far from being homogeneous, in contrast with the assumption introduced in the SCRF model. In fact, one should not forget that the C=O bond was the vibrational probe used to arrive to the above estimate of the effective dielectric constant, and so it is the immediate neighbourhood of this bond that matters more, in spite of the fact that the aromatic ring included in the βCD cavity affects also the C=O stretching frequency through conjugation.

If a previously determined correlation between $\Delta\nu$C=O and the hydrogen bonding enthalpy ($-\Delta H \approx \Delta\nu C{=}O/2 + 5$) [4] is used for Bnz and Bnz-βCD, and the above estimated value of $\Delta\nu_{sp}$ introduced, then it can be concluded that hydrogen bonding interactions in pure Bnz are stronger than in Bnz-βCD by *ca.* 6-7 kJ mol^{-1}.

METHODS

βCD was kindly offered by Wacker Chemie; Bnz, Van and Cin were obtained commercially from Aldrich. The inclusion complexes were prepared by mixing the substrate with the CD in aqueous solution (dropwise addition of the substrate with strong agitation of the solution). This led to the formation of white precipitates which were filtered and dried for 1-2 days over silica gel. Filtration separated excess CD. If there was excess of the substrate, then this was lost by evaporation. While the substrate rapidly evaporated from the physical mixture suggesting that no complex was formed, little alteration in the Raman spectra and in the weight of the dried precipitates was found after one week, thus pointing to an appreciable stability of the complexes.

Raman spectra of the solid (polycrystaline) samples were recorded on a T64000 Jobin-Yvon Raman system. The light source was a Ar^+ laser (Coherent-Innova, 300-05 model), whose output at 514.5 nm was adjusted to provide 90-100 mW at the sample position. Under the experimental conditions used, the error in frequencies is estimated to be within 1 cm^{-1}. Samples were sealed in Kimax glass capilary tubes with inner diameter 0.8 mm. The Raman spectra of the guest-host complexes presented significant differences, both in the spectral features of the guest and of the CD molecules.

A self-consistent reaction field (SCRF) calculation [4] was carried out for Bnz in media of different dielectric constants, using *Gaussian 92* [4] and the 6-31G* basis set. The SCRF method is based on Onsager's reaction field theory. [4] In this model, the solute is placed in a cavity immersed in a continuous medium with a dielectric constant ε. The dipole moment of the solute will induce a reflection dipole in the medium. The resulting reaction (electric) field in the solvent will in turn interact with the molecular dipole leading to net stabilization.

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