UV and IR laser spectroscopy of isolated molecular structural dynamics
Smolarek, S.D.

Citation for published version (APA):
Smolarek, S. (2011). UV and IR laser spectroscopy of isolated molecular structural dynamics

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: http://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.
Chapter 7

Vibrational and electronic spectroscopy of the 4-hydroxystyrene-CO$_2$ cluster and its hydrate: a para-coumaric acid impostor

ABSTRACT

We report on the results of high-resolution spectroscopic studies on the 4-hydroxystyrene-CO$_2$ cluster. We show that these clusters are generated upon heating of para-coumaric acid, the chromophore of the Photoactive Yellow Protein (PYP), as the result of a thermal decarboxylation process. Since the mass of the cluster and the starting material are the same, standard mass-resolved multiphoton ionization spectroscopic methods do not suffice to distinguish these clusters from para-coumaric acid. Instead, more advanced methods that include various UV and IR depletion methods need to be applied. These methods, in combination with quantum chemical calculations, enable us to unravel the structural and spectroscopic properties of 4-hydroxystyrene-CO$_2$ as well as of its hydrate, 4-hydroxystyrene-CO$_2$-H$_2$O.

7.1 Introduction

The Photoactive Yellow Protein (PYP), originally discovered over 20 years ago in the Halorhodospira halophila bacterium [1], is responsible for blue-light avoiding behavior of this organism. Due to its relatively small size (14kDa), water solubility, simplicity in crystal growth, and chemical and photostability, PYP has become during the past two decades a well-established model system for studying the photochemistry that is associated with the conversion of photon energy into biological function, as well as for obtaining a better understanding of protein folding processes. The chromophore responsible for light absorption in PYP is the deprotonated para-coumaric acid (pCA) molecule which is covalently attached to a cystine residue of the protein by a thioester bond. This system has been the subject of a large number of theoretical [2] and
experimental studies [3]. In particular the neutral \( p \)CA molecule has been one of the big challenges for spectroscopists. For a long time \( p \)CA remained out of reach from high-resolution spectroscopy and only derivatives like 4-hydroxystyrene [4] - alternatively designated as \textit{para-}vinylphenol (\( p \)VP), a designation that in view of its use in previous publications will be used here as well - and the oxy-ester methyl-4-hydroxy cinnamate (OM\( p \)CA) [5] were studied.

Recently, we were able to establish a breakthrough when we reported the first high-resolution excitation and absorption spectra of \( p \)CA [6]. In these studies we also observed another band system when performing mass-resolved ion detection at the molecular mass of \( p \)CA that clearly originated from the \( p \)CA sample. In the present studies we show that this one-color Resonance Enhanced MultiPhoton Ionization (REMPI) spectrum originates from clusters of \( p \)VP and \( CO_2 \). Previously, it has been shown [4, 7] that in experiments in which \( p \)CA is heated to acquire a high enough vapor pressure for molecular beam experiments, one readily observes the excitation spectrum of \( p \)VP. In view of the dependence of the intensity of the signals in this spectrum on the temperature of the sample, it was at that time inferred that \( p \)VP was generated from \( p \)CA by a thermal (as opposed to photochemical) decarboxylation process. The present studies provide direct proof for this process. This is a thus very interesting case in which a molecule is dissociated into two products that subsequently form a cluster with an identical mass as that of the starting material.

Apart from elucidating the chemical processes occurring in \( p \)CA, the study of the photochemical and photophysical properties of the \( p \)VP-CO\(_2\) cluster is an interesting subject in its own right. In principle, CO\(_2\) can occupy various binding sites depending on the competition between hydrogen bonding interactions of CO\(_2\) with the phenolic OH group and van der Waals interactions with other parts of the molecule. Similarly, the mixed cluster of \( p \)VP with CO\(_2\) and H\(_2\)O is of interest in terms of the competition for binding sites between CO\(_2\) and H\(_2\)O. Here, we will employ various UV-UV and IR-UV double resonance techniques in combination with quantum chemical calculations to address these issues.

### 7.2 Experimental and theoretical methods

Monomers of \( p \)VP and of its clusters with CO\(_2\) and H\(_2\)O were studied using Resonance Enhanced Multi Photon Ionization (REMPI) spectroscopy, UV depletion (UV-D) spectroscopy, as well as IR depletion (IR-D) and IR hole burning (IR-HB) spectroscopy. These experiments were performed in a setup designed to perform laser spectroscopy on molecules cooled in a supersonic free jet expansion. The molecular beam is created in this setup with an injector assembly that consists of a stainless-steel
oven in which a glass container with the sample is placed. For the present experiments a temperature of 160 °C was used. The oven is connected to a pulsed valve (General Valve Iota One system) equipped with a 0.5 mm diameter nozzle that is typically kept 5 °C above the oven temperature to prevent clogging of the nozzle. Typically, a pulse duration of 220 µs is used. In the present experiments neon at a backing pressure of 1.5-2.5 bar was led through the oven and expanded through the nozzle into the vacuum chamber. After passing through a skimmer with a diameter of 1 mm, the molecular beam is introduced into the ion source region where mass-resolved ion detection is performed using a reflectron type time-of-flight spectrometer (R.M. Jordan Co.).

REMPI excitation spectroscopy was performed in the 33000-34000 cm⁻¹ range using the frequency-doubled output of a dye laser system (Sirah Precision Scan) operating on Rhodamine 610 or a mixture of Rhodamine 590 and Rhodamine 610, and pumped by a 30 Hz Nd:YAG laser (Spectra Physics Lab 190). Typical pulse energies of 2-3 mJ were used without further focusing of the laser beam. To investigate whether the recorded REMPI spectra contained contributions from more than one conformation, we used UV-D spectroscopy [8]. UV-D spectroscopy monitors the signal from a probe laser that is fixed at the frequency of one particular band in the excitation spectrum, and is associated exclusively with a single conformation. Scanning the pump laser then leads to a depletion of this signal as a result of the depopulation of the ground state each time the pump laser is in resonance with a transition of the selected conformer. The probe beam for these UV-D experiments was generated by an excimer-pumped (Lambda Physik CompexPro 205) dye laser (Lumonics HD500). Pump and probe beams were introduced in a counter-propagating fashion into the ionization region with a time delay between the two beams of 100 ns. Typical pulse energies of 4 and 1 mJ were used for the pump and probe beam, respectively. Both laser beams were partially focused by a lens with a focal length of 50 cm placed at 25 cm from the intersection with the molecular beam.

For the IR-D and IR-HB experiments the pump beam in the range of 3422-3760 cm⁻¹ and with an energy per pulse of 1.7 mJ was produced by difference frequency mixing of the output of the dye laser operating on LDS 759 (760-778 nm) with the fundamental of the Nd:YAG laser in a LiNbO₃ crystal. The beam was partially focused by a lens with a focal length of 0.3 m that was placed at a distance of 0.2 m from the intersection with the molecular beam. The UV probe beam with a typical pulse energy of 2 mJ was delayed by 100 ns and partially focused in the same way as in UV-D experiments. During IR-D measurements the UV probe beam was fixed at one particular vibronic transition while the IR pump beam was scanned to obtain a conformer-specific IR absorption spectrum. In case of the IR-HB experiments the IR pump beam was parked on a particular IR band and triggered at half the repetition rate of the UV probe laser of which the wavelength was scanned. During the data analysis signals with and without the
IR pump beam were subtracted from each other, allowing to record IR-selected, conformation-specific excitation spectra with an enhanced signal-to-noise ratio.

\( p \text{CA} \) (98% purity) was purchased from Sigma-Aldrich while \( p \text{VP} \) (99%) was obtained from Apin Chemicals Ltd.. Both samples were used as received without further purification. Heating of \( p \text{CA} \) in the sample reservoir enabled the recording of spectra with a sufficiently high signal-to-noise ratio for the \( p \text{VP}-\text{CO}_2 \) cluster without further measures. However, to confirm that the source of resonance enhancement at a mass of 164 a.m.u is indeed the \( p \text{VP}-\text{CO}_2 \) cluster, experiments were also performed under conditions in which \( \text{CO}_2 \) was added controllably to the neon carrier gas. Experiments on the \( p \text{VP}-\text{CO}_2-\text{H}_2\text{O} \) cluster required explicit addition of water vapor to the carrier gas to obtain acceptable signal-to-noise ratios. In these experiments we employed controlled partial pressures of \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) to avoid the effects of fragmentation from larger clusters.

Quantum chemical calculations on the equilibrium geometry and the harmonic force field of \( p \text{VP} \) and the \( p \text{VP}-\text{CO}_2 \) complex in their electronic ground state were performed with second-order Møller–Plesset perturbation theory (MP2) within the resolution-of-the-identity (RI) approximation [9]. Dunning’s correlation-consistent valence polarized double-zeta basis set (cc-pVDZ) was employed [10]. To find stable minima on the potential energy surface of the cluster, several trial structures characterized by a different arrangement of \( \text{CO}_2 \) with respect to \( p \text{VP} \) were generated that served as input for a preliminarily optimization at the density functional theory (DFT) level using the B3LYP functional [11] and a 6-31G* [12] basis set. These preliminarily optimizations resulted in only three stable structures of which the geometry was further optimized at the MP2 level. For each optimized geometry a normal mode analysis was performed to ensure that it corresponded to a minimum on the potential energy surface. The energies of the complexes were corrected for basis set superposition errors using the function counterpoise correction method [13]. DFT calculations were performed with the Gaussian03 package [14], for MP2 calculations the TURBOMOLE 5.9 suite of programs was employed [15].
7.3 Results and discussion

7.3.1 pVP-CO\textsubscript{2} cluster

Figure 7.1 reports the mass-resolved REMPI excitation spectra recorded at the m/e=164 and m/e=182 channels. We emphasize that in both cases pCA has been employed as a sample source. Although m/e=164 matches the mass of pCA, the spectrum in Figure 7.1a is quite different from the one reported previously [6]. That particular spectrum was shown unambiguously to derive from pCA by IR-D spectroscopy in combination with quantum chemical calculations. On the other hand, the spectrum in Figure 7.1a is very similar to the spectrum observed for the pure pVP sample as reported by de Groot et al. [4, 7], albeit that it is shifted by +106 cm\textsuperscript{-1} to higher excitation energies.

![Figure 7.1](image_url)

**Figure 7.1.** One-color REMPI excitation spectra obtained at (a) m/e=164 and (c) m/e=182 using pCA as a sample. Spectrum (b) has been obtained at m/e=164 as well, but in this case pVP has been used as sample source, while CO\textsubscript{2} has been added to the neon carrier gas. The origin transition appears in (a) as a splitted resonance at 33306 cm\textsuperscript{-1} and 33310 cm\textsuperscript{-1} (see inset), in (c) an apparent single origin transition is observed at 33131 cm\textsuperscript{-1}.

In view of the mass and the spectral similarity, we therefore attribute the signal at m/e=164 to the pVP-CO\textsubscript{2} cluster. Further support and confirmation of this conclusion is provided by additional experiments on pVP, the vibronic activity in the excitation
spectrum, and the IR-D spectrum (*vide infra*). The observed blue shift matches well observations for other CO₂ clusters of benzene derivatives. For example, the phenol-CO₂ cluster has its origin displaced by +38 cm⁻¹ [16], in case of styrene a shift of +51 cm⁻¹ is observed [17]. Similarly, we find that the spectrum detected at m/e=184 (Figure 7.1c) is also reminiscent of the pVP spectrum, although now a red shift of -79 cm⁻¹ is observed. Mass and spectrum appearance lead us to assign this signal to the hydrate of the pVP-CO₂ cluster.

To confirm that the pVP-CO₂ cluster is indeed the carrier of both spectra, we performed measurements on a pure pVP sample in the presence and absence of CO₂ in the Ne carrier gas. In these experiments a signal at m/e=164 was only observed when CO₂ was added to the carrier gas. The spectrum that was obtained under such conditions is shown in Figure 7.1b. Although the spectra in Figures 7.1a and 7.1b have a different signal-to-noise ratio as a result of difficulties in sustaining a stable CO₂ flow, the two spectra are clearly identical. In particular, we notice the activity of low-frequency vibrations and the broad structure in the origin region that can be observed in both cases. This decisively confirms the source of the signal recorded for the pCA sample as being the pVP-CO₂ cluster. The conclusion that the underlying chromophore in all spectra is pVP implies that the overall ionization process is a one-photon Resonance Enhanced Two Photon Ionization (R2PI) process.

The linewidths observed for the sharp resonances in Figure 7.1a are similar to the ones observed for pVP, and are determined by the rotational envelope at the temperature in the supersonic expansion [4b]. Differences with the pVP excitation spectrum are the low-frequency bands at 29 and 91 cm⁻¹ that accompany each of the pVP-type bands. We attribute these bands to intermolecular modes involving both pVP and CO₂. In Figure 7.1a one can also observe a very broad, reproducible structure in the 33290-33450 cm⁻¹ range, a feature that is absent in the pVP spectrum. Similar observations have been made for the phenol-CO₂ cluster [16], where this feature has been attributed to the dissociation of higher-order clusters. We will discuss this issue further below in the context of IR-D and IR-HB experiments performed on the cluster (*vide infra*).

The excitation spectrum of pVP displays a splitted origin band with the two components separated by about 4 cm⁻¹ [4]. A similar splitting has been observed for the origin bands of OMPpCA [5] and pCA [6], and has been attributed to the syn and anti orientations of the OH group. For the pVP-CO₂ cluster a splitted origin band with an energy separation of about 3 cm⁻¹ is observed as well. UV-D experiments shown in Figure 7.2 confirm that these two bands are associated with two distinct conformations. Their depletion spectra are shifted to a minor extent with respect to each other and almost identical in vibrational structure. The only difference well visible is the energy separation between the closely neighboring lines in the 33680 cm⁻¹ region. UV-D experiments on OMPpCA and pCA have shown that for these molecules other conformations involving the
s-trans configuration are present as well. For the pVP-CO₂ cluster such conformations are not possible. Additional hole burning measurements performed for all bands visible in the R2PI spectrum show indeed that all sharp bands in the R2PI spectrum can be attributed to one of the two previously identified conformations, and thus that there are no other conformations present.

Figure 7.2. UV-D spectra of the REMPI signal observed at m/e=164. In (a) the REMPI excitation spectrum is shown, (b) and (c) display depletion spectra obtained when the probe laser is set at the two components of the splitted origin line in (a), 33306 and 33309 cm⁻¹, respectively.

Unfortunately, the UV-D spectra do not enable us to verify whether the broad structure visible in the REMPI spectrum in the 33290-33450 cm⁻¹ region is associated with one of the assigned conformations, or whether it should be attributed to, for example, the dissociation of higher-order clusters. To further investigate this issue and to obtain more information on the conformational structure of the observed species - including the binding site of CO₂ -, we investigated the infrared absorption spectrum of the ground state in the OH stretch region by means of IR-D spectroscopy (Figure 7.3). Figure 7.3 shows that within our experimental resolution the syn and anti conformations give rise to identical IR spectra. For both conformations we observe a strong absorption band at 3650 cm⁻¹ and two weaker lines at 3606 cm⁻¹ and 3712 cm⁻¹. The IR spectrum of pCA [6], OMpCA [18] and phenol [16] exhibits a strong absorption band at 3652, 3652, and 3657 cm⁻¹, respectively, that was assigned to the phenolic OH stretch mode. We
consequently assign the band at 3650 cm\(^{-1}\) in Figure 7.3a and 7.3b to the same mode in the pVP-CO\(_2\) cluster. IR spectra of the bare pVP molecule are not available.

Figure 7.3. IR-D spectra of the two different conformations of pVP-CO\(_2\) associated with the origin transitions at (a) 33306 and (b) 33309 cm\(^{-1}\).

Nevertheless, comparing the OH stretch frequency in bare pCA and phenol with the frequency in pVP-CO\(_2\) suggests that clustering of pVP with CO\(_2\) leads only to a minor shift of the OH stretch frequency, probably around -2 cm\(^{-1}\). For phenol the analogous absorption line is shifted by -26 cm\(^{-1}\) upon CO\(_2\) clustering into a configuration with a hydrogen bond between CO\(_2\) and the OH group [16]. This suggests a much weaker binding character of CO\(_2\) to pVP, or even a different binding configuration between the two components of the cluster.

Assignment of the bands at 3606 and 3712 cm\(^{-1}\) seems more problematic since they cannot be attributed to other OH stretch vibrations. Interestingly, we notice that two similar bands have been observed in the IR spectrum of the phenol-CO\(_2\) cluster [16]. In that particular study, only the band at 3718 cm\(^{-1}\) was discussed and attributed to the combination band of the OH stretch vibration and an intermolecular vibration of CO\(_2\) and
phenol. Such an explanation would still not account for the 3606 cm\(^{-1}\) band in the present study. We therefore propose an alternative explanation. In pure, gaseous CO\(_2\) IR absorption lines are observed at 3610 cm\(^{-1}\) and 3717 cm\(^{-1}\) [19] that have been attributed to the combination band of the symmetric and asymmetric C=O stretch vibrations and the combination band of the asymmetric C=O stretch vibration with the overtone of the bend vibration [20]. We thus assign the bands observed in our experiments at 3606 cm\(^{-1}\) and 3712 cm\(^{-1}\) to the analogous combination bands of CO\(_2\) in the pVP-CO\(_2\) cluster. To confirm that all observed R2PI bands originate from the two previously identified conformations and that they all have the same IR spectrum, IR-HB experiments were performed in which the IR pump frequency was fixed at either 3650 cm\(^{-1}\) or 3712 cm\(^{-1}\) while the frequency of the UV probe laser was scanned (Figure 7.4). The absorption band at 3606 cm\(^{-1}\) could not be employed as a pump because of its low IR absorption cross section. Figure 7.4 shows that for all sharp bands in the R2PI excitation spectrum the IR bands at 3650 and 3712 cm\(^{-1}\) are active.

Figure 7.4. Comparison of IR-HB spectra of the pVP-CO\(_2\) cluster (b and c) with the R2PI excitation spectrum detected at m/e=164 (a). In (b) the IR pump beam is tuned to the IR absorption band at 3650 cm\(^{-1}\) assigned to the phenolic OH stretch vibration. In (c) the IR pump beam is tuned to the IR absorption band at 3712 cm\(^{-1}\) assigned to the combination band of the asymmetric C=O stretch vibration with the overtone of the bend vibration of CO\(_2\) in the pVP-CO\(_2\) cluster.

The broad resonance structure accompanying the sharp resonances visible in the R2PI excitation spectrum is not visible in Figures 7.4a and 7.4b. The absence of this
feature indicates that it is associated with other species than the \( p \text{VP-CO}_2 \) cluster. Further information on the nature of these species can be obtained by careful inspection of Figure 7.3. This Figure shows that the three IR absorption bands observed for the two origin transitions split up and become red-shifted by about 6 cm\(^{-1}\) when the broad resonance structure in the 33290-33450 cm\(^{-1}\) region is probed at 33324 cm\(^{-1}\). To minimize the influence of a non-resonant probe signal arising from the two previously identified \( p \text{VP-CO}_2 \) conformational transitions, IR-D measurements were also performed for UV probe frequencies below the two origin transitions. Such measurements led to the same results as for the 33324 cm\(^{-1}\) probe frequency. The observed splitting and red-shift suggest that several species contribute to the observed R2PI signal. This conclusion is consistent with previous suggestions in the REMPI study on phenol-CO\(_2\) clusters where the broad background in the excitation spectrum was attributed to higher order clusters [16]. For the present study this implies that higher order \( p \text{VP}-(\text{CO}_2)_n \) clusters are responsible for the broad background, and show up in the m/e=164 mass channel because of dissociation of the cluster after ionization.

From a comparison of the phenolic OH stretch frequency in \( p \text{VP-CO}_2 \) and phenol-CO\(_2\) we concluded above that the binding strength and/or configuration of CO\(_2\) to \( p \text{VP} \) is different from that of CO\(_2\) to phenol. To elucidate the characteristics of the binding between CO\(_2\) and \( p \text{VP} \) quantum chemical calculations have been performed. Geometry optimization of the cluster in its electronic ground state and subsequent calculation of the harmonic force field lead to the identification of three stable minima on the \( \text{S}_0 \) potential energy surface with comparable energies (Figure 7.5). Conformation 1 is characterized by a CO\(_2\) molecule located in the plane of \( p \text{VP} \) with a distance of 2.81 Å between the phenolic oxygen and the carbon atom of CO\(_2\). In conformation 2 one of the carbon dioxide oxygen atoms forms a hydrogen bond with the phenolic OH with an O–H distance of 2.4 Å. Conformation 3 is characterized by a CO\(_2\) molecule located above the single C-C bond at a distance of about 3.2 Å in a configuration in which the O=C=O bonds are perpendicular to the C-C bond. The relative energies of these conformations with entropy correction at room temperature are reported in Table 7.1, while the frequencies of relevant vibrations are given in Table 7.2.

![Figure 7.5. Lowest energy structures of the pVP-CO\(_2\) cluster at the MP2/cc-pVDZ level.](image-url)
Table 7.1. Relative enthalpies (cm\(^{-1}\)) at 0 K and free Gibbs energies (cm\(^{-1}\)) at 300 K of lower-energy conformations of pVP-CO\(_2\) clusters.

<table>
<thead>
<tr>
<th>Structure</th>
<th>(\Delta H) 0 K</th>
<th>(\Delta G) 300 K, 1bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>160</td>
<td>250</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>190</td>
</tr>
</tbody>
</table>

Table 7.2. Calculated and measured frequencies (cm\(^{-1}\)) of selected vibrational modes in pVP-CO\(_2\) clusters. Frequencies in parentheses are scaled by a factor of 0.953, taken to reproduce the experimentally observed OH stretch frequency.

<table>
<thead>
<tr>
<th>Structure</th>
<th>CO(_2) bend ((b))</th>
<th>CO(_2) sym. stretch ((s))</th>
<th>CO(_2) asym. stretch ((a))</th>
<th>overtone ((a+2b)^{(b)})</th>
<th>OH stretch</th>
<th>overtone ((a+s)^{(b)})</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Structure 1</td>
<td>Structure 2</td>
<td>Structure 3</td>
<td>Exp.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO(_2) bend ((b))</td>
<td>638 (608)</td>
<td>643 (613)</td>
<td>638 (608)</td>
<td>668(^{(a)})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO(_2) sym. stretch ((s))</td>
<td>1331 (1268)</td>
<td>1329 (1267)</td>
<td>1329 (1267)</td>
<td>1388(^{(a)})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO(_2) asym. stretch ((a))</td>
<td>2444 (2329)</td>
<td>2439 (2324)</td>
<td>2438 (2323)</td>
<td>2350(^{(a)})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>overtone ((a+2b)^{(b)})</td>
<td>3720 (3545)</td>
<td>3725 (3550)</td>
<td>3714 (3539)</td>
<td>3610(^{(a)})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH stretch</td>
<td>3831 (3651)</td>
<td>3819 (3640)</td>
<td>3830 (3650)</td>
<td>3650(^{(c)})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>overtone ((a+s)^{(b)})</td>
<td>3775 (3598)</td>
<td>3768 (3591)</td>
<td>3767 (3590)</td>
<td>3717(^{(a)})</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{(a)}\) Taken from [20], frequencies refer to uncomplexed CO\(_2\).

\(^{(b)}\) Calculated in the harmonic approximation from fundamental frequencies.

\(^{(c)}\) As determined in the present study for the pVP-CO\(_2\) cluster.

Table 7.1 suggests that conformation 1 is the energetically preferred conformation, but at the same time it is clear that one should be very cautious in view of the level of accuracy that can be reached with these types of calculations. In fact, for all practical purposes the three conformations should be considered as having about the same energy. The frequency calculations (Table 7.2) are in this respect more useful since the frequency of the OH stretch mode is a sensitive probe for hydrogen bonding interactions. Previously, we have argued that the experimentally observed shift of this mode upon complexation with CO\(_2\) most probably is within a range of 2 cm\(^{-1}\). In structure 3 the CO\(_2\) molecule is positioned on the ethylenic double bond and thus does not interact with the OH group. Accordingly, one expects that the OH stretch frequency is not affected. This expectation is nicely reproduced by calculations on the pVP monomer for which a frequency of 3830 cm\(^{-1}\) is found. Similarly, we also find for structure 1 that the OH stretch frequency is hardly changed (a blue shift of 1 cm\(^{-1}\) is calculated). For structure 2, in contrast, the calculations predict a much larger shift of ~10 cm\(^{-1}\). These observations thus indicate that the cluster observed in our experiments has either structure 1 or
structure 3. In passing by, we notice from Table 7.2 that the frequencies calculated for the combination bands are shifted significantly to the red compared to the experiment when the same scaling factor is used for the combination bands as for the OH stretch. Inspection of this Table shows that the main reason for the red shift is the failure of the calculation to reproduce the experimental frequencies of the symmetric C=O stretch and the bend vibration in CO₂.

7.3.2 pVP-CO₂-H₂O cluster

Figure 7.1b displays the R2PI excitation spectrum detected at m/e=182 that we have assigned to the pVP-CO₂-H₂O mixed cluster. The origin of the excitation spectrum is located at 33131 cm⁻¹ and is shifted by -175 cm⁻¹ with respect to the pVP-CO₂ cluster. This shift is only about half of what is observed for phenol [21] but nevertheless still so large that one has to conclude that H₂O is directly bound to pVP and not indirectly via CO₂. The vibrational activity in the excitation spectrum of both clusters is similar, yet some clear differences are observed. These relate to low-frequency vibrations associated with intermolecular modes. For the pVP-CO₂ cluster bands are found at 29 cm⁻¹ and 91 cm⁻¹, while in the mixed cluster these frequencies change to 36 cm⁻¹ and 64 cm⁻¹. Additionally, the mixed cluster shows a broad band ~160 cm⁻¹ above the origin that is absent in the pVP-CO₂ cluster. Interestingly, in the excitation spectrum of phenol-H₂O a relatively strong band is observed at 156 cm⁻¹ that has been assigned to the hydrogen bond stretch vibration between phenol and H₂O [22]. We therefore conclude that H₂O is hydrogen bonded in a similar way to pVP as it is in phenol, and that in both complexes the hydrogen bond strength in S₁ is rather similar. This conclusion is confirmed by IR absorption spectra that will be discussed below.

Another striking difference between the R2PI spectra of pVP-CO₂ and pVP-CO₂-H₂O concerns the widths of the resonances. For the pVP-CO₂ cluster widths of ~1.5 cm⁻¹ are found, whereas for pVP-CO₂-H₂O they are close to 10 cm⁻¹. Lifetime broadening can be excluded since the implied excited-state lifetime of ~0.5 ps would in that case significantly reduce the probability for R2PI with a nanosecond laser. Assuming that the pVP-CO₂ and pVP-CO₂-H₂O concentrations are of the same order of magnitude, and that the oscillator strengths in the two complexes are also about the same, this would be at odds with the experimental observation that the pVP-CO₂ and pVP-CO₂-H₂O signals are of comparable magnitude. We therefore attribute the linewidths to inhomogeneous broadening as the result of the presence of a relatively large number of cluster conformations.

Our conclusion that H₂O is hydrogen bonded to the phenolic OH group in the pVP-CO₂-H₂O cluster is confirmed by the observed IR-D spectra (Figure 7.3d). In the
pVP-CO₂ cluster we have seen that the OH stretch frequency remains practically undisturbed by the presence of CO₂. In the pVP-CO₂-H₂O cluster, on the other hand, the OH stretch band appears as a splitted resonance at 3465 and 3472 cm⁻¹, and is thus shifted by about -195 cm⁻¹. For phenol the OH stretch frequency is only reduced by 133 cm⁻¹ (from 3657 to 3524 cm⁻¹) upon complexation with water [23], indicating that pVP is a better proton donor than phenol. The splitting of the OH stretch band suggests the presence of multiple conformations. IR-HB experiments with the IR pump beam tuned to each of the two bands, however, does not lead to distinguishable excitation spectra, but merely reproduce the R2PI spectrum displayed in Figure 7.1b. A possible explanation for these observations is that the two or more conformations associated with the two IR bands have nearly identical excitation spectra such that possible excitation energy differences between analogous bands are smaller than the linewidths observed in Figure 7.1b. Logical candidates for these conformers are the two OH syn and anti conformers. In the pVP-CO₂ cluster the origin transitions of these two conformations differ by 3 cm⁻¹ (vide supra). If a similar separation is maintained in the pVP-CO₂-H₂O cluster, the two lines would fall within the observed 10 cm⁻¹ linewidth and not be distinguishable.

Figure 7.3d shows that the bands assigned to combination bands of CO₂ vibrations are slightly red-shifted compared to pVP-CO₂. Bands are now found at 3602 and 3711 cm⁻¹ instead of 3606 and 3712 cm⁻¹. From the small but distinct shifts of these bands we tentatively conclude that in the mixed cluster CO₂ and H₂O are located in close proximity, and not on different parts of the molecules as would, for example, be the case if the pVP-CO₂ configuration would be similar to conformation 3 in Figure 7.5. The two bands observed at 3734 and 3633 cm⁻¹ in Figure 7.3d are assigned to the asymmetric and symmetric OH stretch vibrations of H₂O. Interestingly, in the IR absorption spectrum of the phenol-H₂O complex the asymmetric OH stretch appears as a relatively strong band at 3748 cm⁻¹, while the symmetric OH stretch is too weak to be observed. Ionization detected stimulated Raman spectroscopy [24] has determined its frequency to be 3650 cm⁻¹. Notice that in the free water molecule the asymmetric and symmetric OH stretch vibrations have frequencies of 3756 and 3657 cm⁻¹, respectively, and a much larger absorption cross section for the asymmetric mode than for the symmetric one. Clustering of H₂O to phenol thus affects these two modes only to a minor extent, both with respect to frequency as well as intensity in the IR absorption spectrum. However, the frequency shifts observed in the pVP-CO₂-H₂O cluster (-22 and -24 cm⁻¹ for the asymmetric and symmetric modes) as well as the relatively large intensity of the symmetric stretch show that in this cluster significantly larger changes occur in the electronic structure of H₂O.
7.4 Summary

In the present experiments we have investigated mass-resolved REMPI spectra observed when pCA is taken as sample source. The molecular mass of pCA is 164 a.m.u., and one would therefore most logically assign the one-color REMPI spectrum observed at m/e=164 to this molecule. Our studies have shown that this assignment is not correct. Careful consideration of the observed REMPI excitation and IR absorption spectra, together with separate studies on pVP under expansion conditions in which CO$_2$ was controllably added, prove unambiguously that the excitation spectrum finds its origin in the cluster of pVP and CO$_2$. We must conclude therefore that in the studies that use pCA as sample, the molecule itself must be the source that provides CO$_2$. Our experiments thus provide direct proof for the importance of a thermal dissociation pathway of pCA into pVP and CO$_2$ that was inferred from our previous experiments [7].

Quantum chemical calculations indicate that the pVP-CO$_2$ cluster can adopt various conformations of comparable energy. The accuracy of the calculations does not enable us to make a definite statement on which conformation is actually observed in the experiments, but a comparison between the observed and predicted IR absorption spectra suggests that a structure in which CO$_2$ lies in the pVP plane and is bound by van der Waals interactions to the phenolic oxygen dominates. In our experiments the hydrate of the pVP-CO$_2$ cluster was observed as well. R2PI excitation and IR absorption spectra show that in this cluster H$_2$O is hydrogen bonded to the phenolic OH. A comparison with the same spectra obtained in the past for the phenol-H$_2$O cluster is informative as it shows that clustering influences the properties of the water molecule appreciably more in the pVP-CO$_2$-H$_2$O cluster than in the phenol-H$_2$O cluster, despite the fact that hydrogen bonding between H$_2$O and the phenolic OH is in both cases the dominant interaction.

Till the recent past, pCA proved to be elusive for high-resolution spectroscopy. One of the reasons underlying this elusiveness is its thermal decarboxylation. As a result, excitation and absorption spectra obtained by spectroscopic techniques that do not allow for mass-resolved detection are dominated by the reaction products. This work shows that also when spectra are obtained in a mass-resolved fashion, one can still be lured into drawing the wrong conclusions. Even when the signal is obtained using pCA as sample source, is detected at the mass of pCA, and has an excitation spectrum in the expected energy range for pCA, it still does not need to originate from pCA.

Acknowledgments

This work was supported by The Netherlands Organization for Scientific Research (NWO).
References


