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Infrared spectroscopy of jet-cooled, electronically excited clusters of Coumarin 151: excited-state interactions and conformational relaxation

Yu Chen, Phillip M. Palmer, Michael R. Topp*

Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323, USA

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Abstract

Infrared-optical double-resonance measurements have been made for electronically excited, hydrogen-bonded clusters involving Coumarin 151 molecules under jet-cooled conditions. Two main differences are reported between the ground and excited states:

1. Infrared resonances attributed to "donor"-OH and -NH bonds, as well as the symmetric-stretch modes of non-hydrogen-bonded NH_2 tend to downshift in energy and are usually intensified in the excited state. Also, "donor"-NH groups tend to develop an additional strong infrared resonance in the excited state, which is observed for clusters of C151 with methanol, ethanol, di-isopropyl ether, and for the "B" conformers of the water $n = 1$, 2 and acetone $n = 1$ clusters. The effect evidently requires no activation energy, since it is observed following electronic-origin excitation. A similar effect is also observed in the doubly-hydrogen-bonded dimers of some aminophthalimide molecules. This result is discussed in terms of possible excited-state proton transfer and Fermi resonance interactions.
2. Several clusters have shown changes in the infrared spectra consistent with vibronically-induced conformational rearrangement. The driving force is the relative stabilization of the NH_2 proton-donor site in the excited state and the formation of a strong $NH\cdots O$ hydrogen bond. The cases noted here are C151/$(H_2O)_2$, C120/$(H_2O)_2$ and C151/$((CH_3)_2CO)_1$. One surprising observation here is that the activation energy for the conformational relaxation of C151/$(H_2O)_2$ is measured to be only $60\,cm^{-1}$, and yet the displacement of the water dimer within the cluster exceeds 7 Å.

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Keywords: Infrared spectroscopy; Jet-cooled; Conformational; Clusters

1. Introduction

Many coumarin derivatives, when electronically excited in fluid solution by short optical pulses, exhibit rapid fluorescence Stokes shifts resulting from large changes in the molecular dipole moment. The complex time dependence of solvent-dependent fluorescence Stokes shifts has led to the wide use of coumarins to probe solvation and energy-transfer phenomena [1–17]. Some species, such as Coumarin 153 (C153), have fluorescence spectra, quantum yields and decay times that vary little in different polar

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* Corresponding author. E-mail: mrt@sas.upenn.edu

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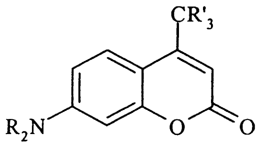
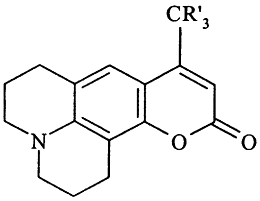
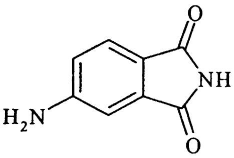
solvents [2,5]. Yet, analysis of the ultrafast solvation response requires different polar solvents to be treated differently by computational models. Thus, acetonitrile is often treated as a quasi-continuous medium, where inertial motions of solvent molecules contribute to the ultrafast relaxation dynamics [18]. On the other hand, successful models for solutions in water and alcohols need to reflect the time scale for hydrogen-bond exchange [19]. Such differences are more evident in the case of 4-aminophthalimide, where hydrogen-bonded interactions promote much larger Stokes shifts than a solvent such as acetonitrile [20–23]. Charge-transfer interactions involving hydrogen bonding solvents are considered to play an important role in the accompanying reduction of the fluorescence quantum yield. The acid–base strength of some coumarins in fluid solution, such as 7-hydroxy-4-methylcoumarin (Coumarin 4) changes greatly between the ground (pK_a ≈ 7) and excited states (pK_a ≈ 0) [24,25]. This suggests that jet-cooled clusters of this and similar coumarin molecules could show significant proton transfer tendencies under jet-cooled conditions. Hydrogen-bonded interactions are difficult to compute, especially in electronically excited states, because such interactions are coupled to the energy level structure of complex molecules. For example, the site of hydrogen-bonded interaction can substantially affect both the energy and radiative properties of low-lying singlet states [26,27]. One must also assume that nearby electronic states are perturbed by solvent–solute interactions and, although coupling between electronic states certainly influences the properties of normal fluorescence, such considerations have received little detailed attention in the literature.



Coumarins 151, 152, 152A
(R=H, CH$_3$, C$_2$H$_5$; R'=F)
Coumarin 120
(R=H; R'=H)



Coumarins 102, 153
(R'=H, F)



4-Aminophthalimide

One such example is that the fluorescence decay time of C152A decreases from >5 ns in non-polar solvents to 230 ps in water [28], an effect that has been attributed to the stabilization of a charge transfer state [2,5]. Aminophthalimides commonly show reduced fluorescence quantum yields in hydrogen bonding solvents, which also implicates possible charge-transfer interactions stemming from hydrogen bonding [22].

An attractive approach to study hydrogen-bonded interactions involves making clusters under jet-cooled molecular beam conditions, followed by infrared double-resonance spectroscopy [29–34]. In this way, one can study clusters close to the zero-point energy condition to simplify the picture of intermolecular interactions, and at selected internal energy to follow controlled relaxation events. Several laboratories have recently employed the infrared-optical double-resonance approach to study the O–H and/or N–H stretch modes of hydrogen-bonded clusters involving aromatic molecules. This includes benzene [32,35–39], phenol [33,34,40–43], aniline [44], other benzene derivatives [45], perylene [46], 1-naphthol [47], indole [48,49], 2-pyridone [50], benzonitrile [51], Coumarins 151 and 152A [27,52,53], the DNA base guanine [54] and dimers of 2-pyridone [50], *N*-benzylformamide [55], 2-phenylacetamide [56] and 4-amino-*N*-methylphthalimide [57]. Ishiuchi et al. [58] also used infrared techniques to analyze the products of photo-induced proton transfer in jet-cooled phenol–ammonia clusters, and work from this laboratory has reported using infrared techniques to observe conformational change in the water dimer cluster of Coumarin 151 [53]. Ultrafast infrared-optical double-resonance experiments have also studied thermally activated hydrogen-bond dissociation following optical excitation of coumarins in binary solvents [19,59–62]. In an increasing number of cases, one can examine parallels in the behavior of condensed-phase and jet-cooled clusters.

Work from this laboratory reported spectroscopic measurements of Coumarins 151, 152A, 153 and 337 as well as some of their hydrogen-bonded clusters with water and methanol [26,27,52,63]. This revealed that coumarins and aminophthalimides [64,65] exhibit very large spectral red shifts (e.g., $>3850\,\mathrm{cm}^{-1}$ for C151/(H$_2$O)$_5$ and $\approx 2495\,\mathrm{cm}^{-1}$ for 4AP/(H$_2$O)$_2$), as indicated in the comparison graph of Fig. 1 [37,64–76]. Moreover, all the clusters indicated for 4-amino-*N*-methylphthalimide (4ANMP) and C151 exhibit well-resolved electronic spectra and infrared double-resonance spectra. This makes these kinds of species particularly attractive to investigate in jet-cooled clusters, considering the large electronic perturbations induced by only a few attached molecules. Other work from this laboratory has shown evidence of the coexistence of different structural forms [26,27,63]. For example, C151/(H$_2$O)$_1$ has two conformers, one involving proton donation by water to the >C=O group (red shift $= 45\,\mathrm{cm}^{-1}$), and the other, proton donation by NH to water (red shift $\approx 690\,\mathrm{cm}^{-1}$) [27]. The observation that the ionization energy of the NH$_2$-bound cluster is lower by $\approx$0.5 eV [26] is a significant measure of how the electronic level structure depends on the location of the hydrogen bond.

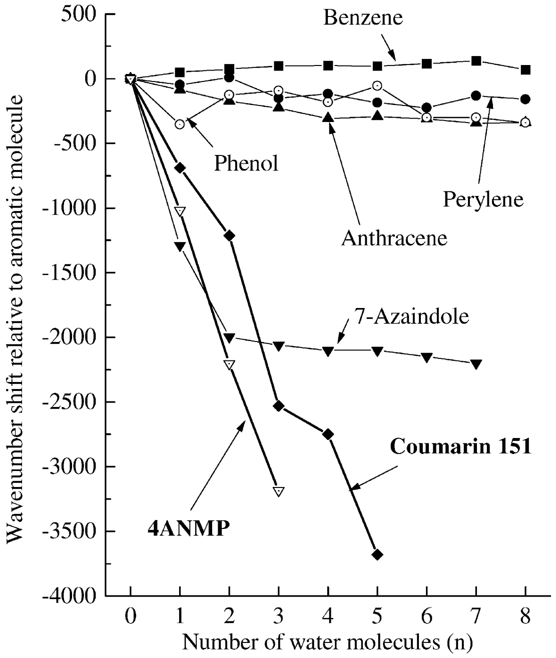


Fig. 1. Comparison of the spectral shifts for water clusters hydrogen bonded to different aromatic molecules. For 4ANMP and C151, where more than one conformer is present, the greater shift is indicated (4ANMP≡4-amino-*N*-methylphthalimide).

In isolated, jet-cooled molecular clusters, both the clustering material and the site of hydrogen-bond attachment to a large molecule can substantially change the energy and radiative properties of the lowest excited singlet states of molecules such as coumarins and aminophthalimides [26,27,64]. For example, the fluorescence decay time of jet-cooled 4-aminophthalimide (4AP) increases by a factor of 3 when hydrogen bonded to a single water molecule, and radiative lifetimes for this class of molecules in polar environments extend to at least 50 ns [64]. This illustrates the sensitivity of not only the S$_1$ state but also the coupling between S$_1$ and other electronic states to the site of hydrogen bonding.

Although the photoisomerization of individual molecules under jet-cooled conditions is well known [77–81], only a few studies have reported photo-induced structural change in weakly bound clusters, especially involving large molecules. Two such cases reported by this laboratory involve perylene 1:1 van der Waals complexes with *n*-alkyl halides [82,83] and *p*-dichlorobenzene [84]. Both studies employed rotational coherence spectroscopy [85] to assign the initial structures in the excited state, but provided no direct information about the products of relaxation. This is because conformational relaxation results in dephasing of the rotational coherence, due to the time dependence of the inertial moments.

In 1998, work from this laboratory showed that the hydrogen-bonded water dimer cluster of Coumarin 151, C151/(H$_2$O)$_2$, undergoes non-radiative relaxation limited by a $60\,\mathrm{cm}^{-1}$ activation barrier [26].

Time-correlated single-photon counting measurements produced evidence of the time evolution of the process, and also showed an increase in the fluorescence decay time from <7 to ≈9.5 ns. At the same time, the ionization threshold decreased by ≈1000 cm^{-1}, showing a pronounced difference in electronic character of the initial and product states. More recent work has shown that this process involves a conformational change between two distinct structures of the cluster [53]. This is an important example of cluster rearrangement triggered by electronic excitation.

In the current paper, we report the results of experiments focusing on the infrared spectra of electronically excited hydrogen-bonded clusters of the molecule C151, to explore the effects of electronic excitation on cluster properties. This includes examples of Fermi resonance interactions, vibronically-induced conformational change and possible proton-transfer interactions.

2. Experimental

All experiments reported here involved a two-pulse excitation–ionization sequence followed by mass-resolved detection via a time-of-flight spectrometer. This served to identify all clusters present in the jet, and also provided an important detection mode for infrared-optical double-resonance measurements. The experiments combined a 10 Hz supersonic jet with a two-chamber differentially pumped vacuum system, using a 2 mm diameter beam skimmer and 70 cm time-of-flight mass spectrometer [27,46,52,53] (see Fig. 2). Sequences of three laser pulses (pulse duration <5 ns) crossed the jet about 10 cm downstream

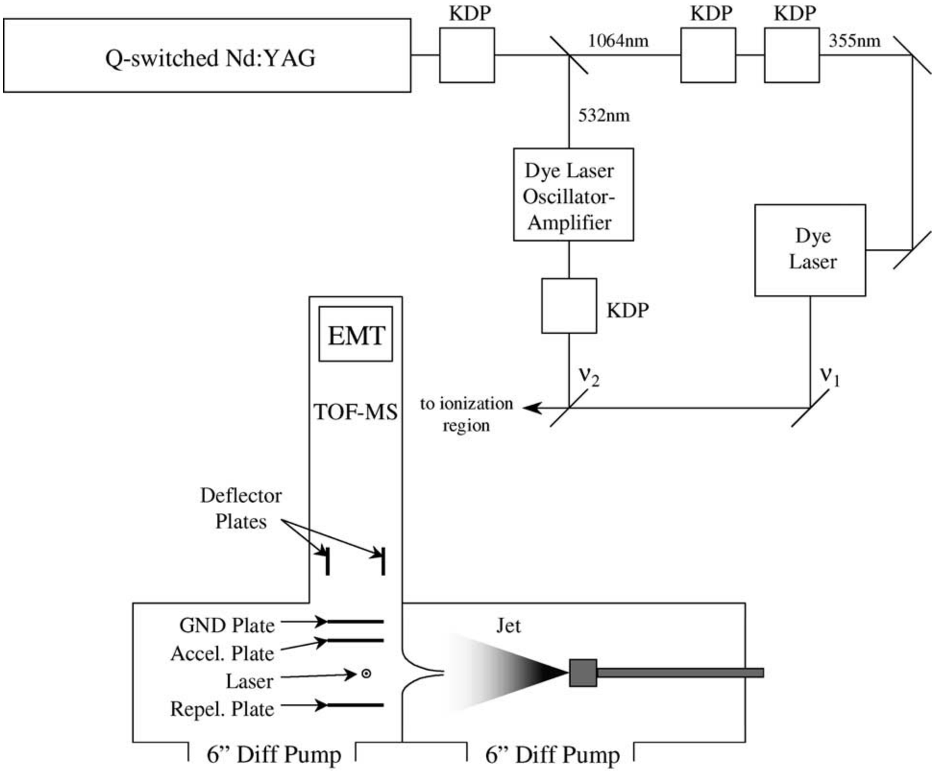


Fig. 2. Schematic diagram of the apparatus used for supersonic jet spectroscopy of clusters, showing the configuration of the chamber and a simple two-pulse pump probe laser arrangement. The infrared generation apparatus is not shown.

from the skimmer orifice, which was in turn located typically 4 cm downstream from the heated nozzle. The supersonic jet used a General Valve Series 9 solenoid valve driven by 160 ms pulses from their Iota One pulse generator. Resonant UV pulses came from LDS 698, 722, 751 or 821 lasers, pumped by 532 nm pulses and frequency-doubled in BBO. For reference, the electronic-origin transitions of the different coumarins are located as follows; C120: 30,075 cm^{-1}; C151: 28,622 cm^{-1}; C152A: 26,849 cm^{-1}; C153: (two conformers) [63] 25,898, 25,710 cm^{-1}. Also, the water cluster red shifts of interest to the present work range from 45 to 2600 cm^{-1}. Nd:YAG fourth-harmonic pulses (266 nm) ionized the electronically excited clusters. For the most part, substitution of 266 nm pulses for a tunable ionization source and near-threshold ionization conditions caused no substantial complications. Water clusters involving C120 readily predissociated one of the water molecules under these conditions, and clusters involving “n” water molecules were usually detected in the “$n-1$” mass channel. We note that a similar observation was reported by Zwier and co-workers for the cluster indole/$(H_2O)_2$ [48]. However, we found that all other clusters could be detected via the parent mass channel. In either case, the species involved could be reliably detected and identified.

Tunable infrared pulses were generated by combining Nd:YAG second-harmonic pulses (532 nm) with amplified DCM dye laser pulses (630–665 nm) in $LiNbO_3$ [27]. Typically, 25 mJ pulses at 532 nm were combined with ≈10 mJ amplified dye laser pulses to yield ≥200 μJ tunable infrared pulses. Ground-state infrared double-resonance spectra were generated from pulse sequences of the type IR–UV–IONIZE, whereas switching the order of infrared and $S_0 \leftrightarrow S_1$ resonant pulses (UV–IR–IONIZE) allowed measurement of the excited-state infrared spectra. To burn efficient excited-state holes, it was necessary to bring the UV and IR pulses as close as possible in time without accidentally detecting ground-state resonances. Using our laser system, even the parent C151 molecule, having an excited-state lifetime of only 3.5 ns readily gave a separable excited-state spectrum. Bringing the infrared pulses last in the sequence (UV–IONIZE–IR) allowed reference experiments to be made of the infrared spectra of cluster cations. This clarified some band assignments.

Detection of the infrared-optical double-resonance signals for C151-based clusters mostly involved ion depletion (i.e., hole burning), using a beam chopping arrangement and simultaneous two-channel detection on the parent mass channel. In this widely used approach, infrared absorption causes a reduction in the parent-ion signal, due to predissociation or other non-radiative processes. Infrared depletion signals ranged from <5 to >90%, using a counterpropagating geometry for the infrared and resonant ultraviolet pulses. Scanning the infrared frequency generates an action spectrum for ion depletion, which is effectively the same as the infrared absorption spectrum [29,35,86]. An important companion technique, which applies to some of the electronically excited clusters, involves detecting the products following infrared-induced predissociation of a water molecule. Although the absolute signal is always less than the amount of signal depletion in the parent channel, this zero-background technique can have a much higher signal-to-noise ratio, and is sensitive to the lifetimes of excited fragment clusters. For example, we used this approach to detect the infrared spectrum of the cluster C151/$(H_2O)_3$, which photodissociates efficiently upon infrared absorption and 266 nm ionization. Wherever the photodissociation technique was used, it was always cross-calibrated against the depletion signal in the same experiment using two boxcar channels.

3. Results and discussion

3.1. Non-hydrogen-bonded cases

3.1.1. Isolated, jet-cooled Coumarin 151

The first reported study of coumarins under jet-cooled conditions was by Ernsting et al. [87]. Consistently with its thermally sensitive weak fluorescence in non-polar solvents [5], the fluorescence excitation spectrum of jet-cooled C151 is found to be

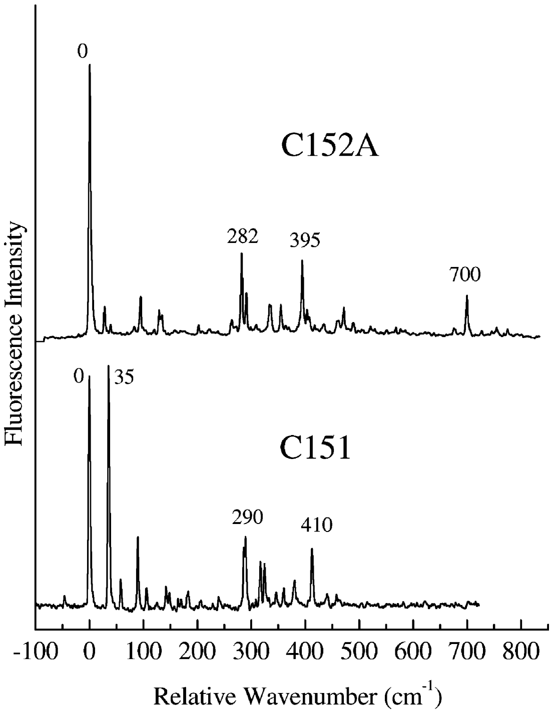


Fig. 3. Comparison electronic excitation spectrum of C151

truncated above a vibrational energy of ≈450 cm^{-1} [87,88]. Unlike C152, C152A, or C153 [87,89], there appears to be facile coupling to the triplet manifold for vibrationally excited S_1 states. Fig. 3 compares the excitation spectrum of jet-cooled C151 with that of the *N*,*N*-diethyl derivative, C152A [26]. For reference, the electronic origin of the $S_0 \rightarrow S_1$ transition in C151 occurs at 28,622 cm^{-1} (349.4 nm). The excitation spectrum, obtained at low laser intensity where saturation is minimal, exhibits several medium to strong vibronic bands up to ≈450 cm^{-1}. In particular, the strong resonance at 35 cm^{-1} is attributed to torsional vibration of the $–CF_3$ group coupled to inversion of the NH_2 group [88]. For the record, we measured the fluorescence decay time following excitation of C151 via an absorption band at +676 cm^{-1}, to be ≈60 ps [26]. The C152A spectrum is simpler, and has the important difference that there is no rapid quenching of excited states at 700 cm^{-1} above the S_1 origin.

The ground-state infrared spectrum of isolated C151 (Fig. 4) has two narrow resonances near 3455 and 3551 cm^{-1}, which may confidently be assigned to the symmetric and antisymmetric stretch normal modes of the NH_2 group. This has been confirmed by semiempirical vibrational mode simulations [27]. In the excited state, the symmetric stretch resonance becomes substantially stronger and broader, slightly downshifted in peak frequency (3455 → 3444 cm^{-1}) and developing an asymmetric profile such that the band degrades slowly to lower energy. This intensification is evidently due to a selective electronic perturbation, since the antisymmetric stretch band is much weaker. Also, the splitting of the two resonances increases from 96 to 113 cm^{-1}, indicating stronger coupling of the zero-order NH-stretch modes in the excited state. In some clusters, the weak higher-energy band was barely detectable with our apparatus.

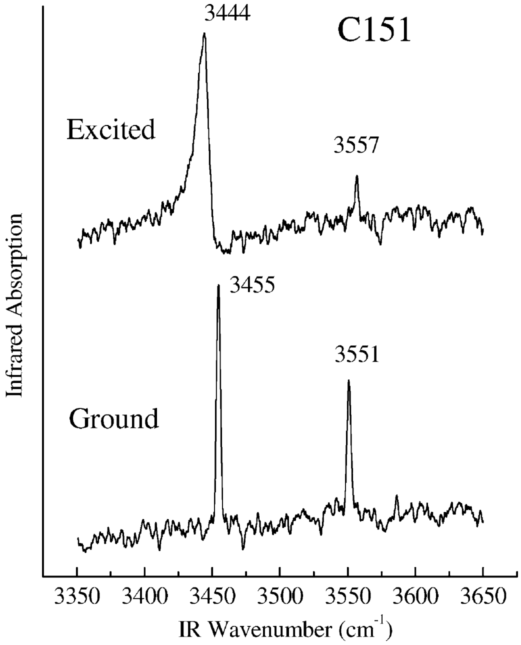


Fig. 4. Ground and excited-state infrared spectra for C151. We found the same spectra for any vibronic resonance probed.

3.1.2. The cluster with acetonitrile—ground and excited-state behavior

A solution of C151 in the polar, non-hydrogen bonding solvent acetonitrile shows almost the same

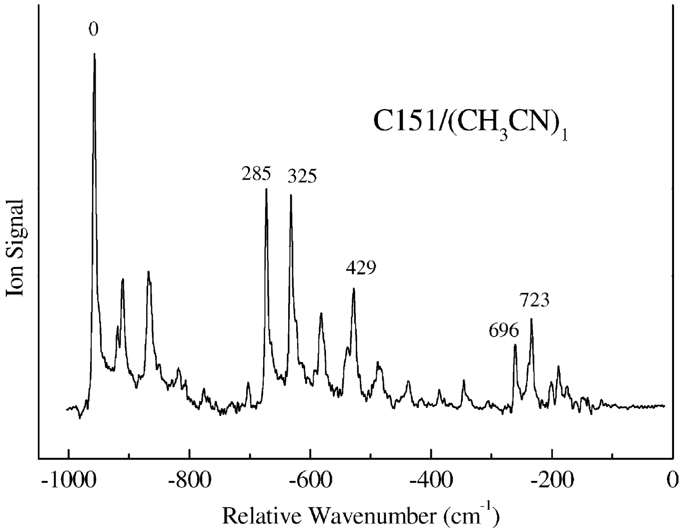


Fig. 5. Electronic excitation spectrum of C151/CH$_3$CN showing the greater extent of vibronic structure, which indicates that the non-radiative channel for C151 is not available in this cluster.

large shifts in the absorption and emission spectra as in hydrogen-bonded alcohol solutions [5]. The jet-cooled 1:1 cluster with acetonitrile (C151/CH$_3$CN) echoes this property, showing a greater red shift (957 cm^{-1}) than the 1:1 ethanol cluster (842 cm^{-1}). Also, the excitation spectrum (Fig. 5) extends over a broader range (>700 cm^{-1}) than C151 itself (see Fig. 3), showing that there is no comparable low-energy non-radiative path to that seen for isolated C151. There are prominent vibronic features in the same general frequency

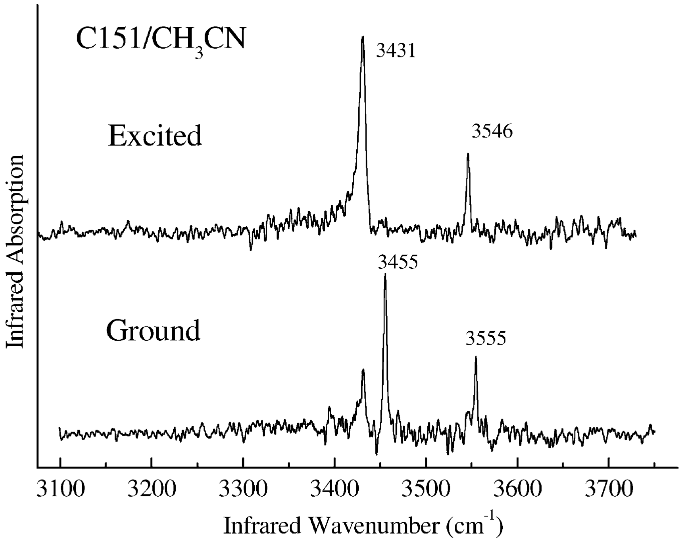


Fig. 6. Ground and excited-state infrared spectra for C151/CH$_3$CN. The infrared bands are similarly placed to C151 itself, and the asymmetric broadening of the 3431 cm^{-1} band is similar to that of C151. Imperfect time separation here caused some cross-talk in the ground-state spectrum.

range as those seen for C151, at 280, 325 and 700/720 cm^{-1}, although the strongest vibronic band in the C151 spectrum, the 39 cm^{-1} feature attributed to a coupled NH_2 inversion and CF_3 torsion [88], is much weaker in the acetonitrile cluster. Despite the substantial perturbation of the electronic structure, the infrared spectrum of the NH_2 normal stretching modes of C151/CH_3CN is similar to that of the bare molecule, in both the ground and excited states (see Fig. 6). This demonstrates both that there is no significant hydrogen bond and that the electronic perturbation of the NH-stretch modes is about the same for both species. At this point, the structure of the cluster has not been calculated, but the data show no evident perturbation of the NH_2 group. Moreover, the obvious change in the relative intensity of the NH_2-stretch normal modes between the ground and excited states appears similar to C151 itself. We therefore conclude that, despite a large electronic perturbation, the presence of an acetonitrile molecule does not strongly perturb the NH-stretch modes. As we show in the next section, hydrogen-bonded interactions cause much larger effects in both the ground and excited states. A final point is that, despite the large red shift of the electronic spectrum, the excited-state infrared spectrum shows no significant features in the range 3100–3400 cm^{-1}. This will be shown in the next section, to be quite different from any of the cases involving hydrogen bonding to the NH_2 group.

3.2. Hydrogen-bonded clusters—multiple conformers in the ground state

Experiments have shown that the C151 molecule uses one of two principal sites in forming hydrogen-bonded clusters. As noted above, the cluster C151/$(H_2O)_1$ exhibits two distinct conformers. One of these involves proton donation by a water molecule to the >C=O group of the α-pyrone ring. This species, which has a red shift of 45 cm^{-1}, is designated the “A” conformer. The other principal site involves proton donation by the NH_2 group to the oxygen atom in a water molecule. This species, having a red shift of 690 cm^{-1}, is designated the “B” conformer. We note that infrared spectroscopy was needed to identify these conformers in the absence of accurate electronic energy calculations [27]. The greater red shift for the “B” conformer is evidence for a significantly greater increase in cluster binding energy at the NH_2 site upon excitation. This may reflect an increase in hydrogen bond strength, although as noted from the behavior of the non-hydrogen-bonded acetonitrile cluster, there should also be a large contribution from the purely electrostatic interaction.

In larger clusters, one might expect a greater number of conformers to occur, leading to increasingly complex electronic spectra. However, for strongly self-aggregating materials such as water and methanol, the problem appears simpler for some larger clusters than in the case of one or two attached molecules. For example, we have detected a single form of the cluster C151/$(H_2O)_5$, characterized by a single infrared spectrum [90]. On the other hand, evidence of multiple conformers for smaller clusters is readily revealed by either electronic or infrared hole-burning techniques [26], of which the infrared approach can more easily reveal functional differences. Thus, both the water $n = 1$ and $n = 2$ clusters of C151 show two conformers. The “A” and “B” conformers of the $n = 1$ species are present in roughly equal amounts, whereas the >C=O attached “A” conformer of the $n = 2$ cluster is the majority species [27,52,53]. On the other hand, alcohols, ethers and acetone at the $n = 1$ level only attach via the NH_2 site on C151, whereas the only conformer we have found for the methanol $n = 2$ cluster is attached via the >C=O group.

At this juncture, it is important to note that we do not have any spectroscopic data from the >C=O stretch region, which could provide definitive proof of proton donation to the >C=O group. However, we do know that some of the clusters exhibit unperturbed NH_2-stretch resonances of C151 in both the ground and excited states, which certainly suggests a >C=O binding site. Also, density functional theory calculations (B3LYP, 6-31G*) readily predict clusters attached via NH proton donation to water or by OH proton donation from water to >C=O with comparable binding energy. None of these calculations favors

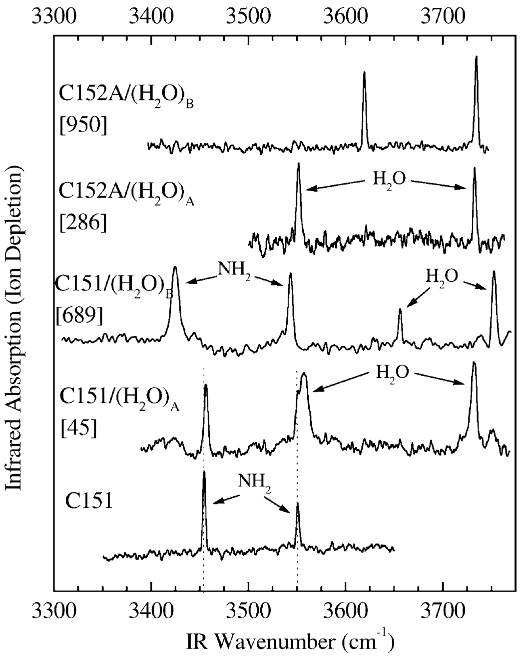


Fig. 7. Sequence of ground-state infrared spectra for water $n = 1$ clusters with C151 and C152A. The quantities in the square brackets indicate the red shifts from C151.

proton donation to the NH_2 nitrogen atom, to the ring oxygen atom or to the aromatic π-electrons. Finally, evidence from condensed phase infrared experiments, which did probe the >C=O stretch region, shows that acidic species such as $CHCl_3$ and phenol both form hydrogen bonds to the >C=O oxygen atom of Coumarin 102 [19,59,61,62].

The bottom trace in Fig. 7 shows the ground-state normal-mode spectrum of the unperturbed NH_2 group of isolated C151. This pair of bands is also evident in the trace for the "A" conformer of C151/$(H_2O)_1$, despite the overlapping resonance from a broadened, displaced OH band of the water molecule. This widely spaced pair of OH resonances is characteristic of water attached to the >C=O group, as may also be seen from the spectra of the "A" conformer of C152A/$(H_2O)_1$. Although the two OH bands correlate with the symmetric (lower) and antisymmetric (higher) resonances of the water molecule, it is perhaps more useful to refer to these, when hydrogen bonded, in local-mode terms as "donor" (lower) and "free"-OH resonances [91]. The "B" conformer of C151/$(H_2O)_1$ shows that, whereas the water molecule is almost unperturbed from the case of free-water, the NH_2 bands are more widely spaced, indicating the presence of a hydrogen bond of the type $NH\cdots O$. The C152A molecule, which is the *N*-diethyl derivative of C151, has no NH bonds. The "A" conformer of C152A/$(H_2O)_1$ shows comparable donor-OH resonances to the C151 counterpart. However, although there is still a large red shift in the "B" conformer ($950\,cm^{-1}$), it is likely that the lower-energy OH resonance at $3620\,cm^{-1}$ represents proton donation either to the nitrogen atom or possibly even to the aromatic ring. For example, the "B" conformer of C151/$(H_2O)_2$ exhibits a resonance at $3602\,cm^{-1}$, which we attribute to proton donation to the aromatic ring [53].

Although infrared studies of the >C=O resonance are needed for definitive assignment, we find that data such as presented in Fig. 7 are sufficient to distinguish between the two sites in C151. In parenthesis, we note that the molecule C120 tends to favor the >C=O site, so that only one conformer is found of the water $n = 1$ cluster, which shows no perturbation of the NH_2 resonances. The same is true for the methanol cluster of C120, in which the methanol molecule is a proton donor to the >C=O group, even though the only observed form of C151/$(CH_3OH)_1$ has an $NH\cdots O$ hydrogen bond. Interestingly, however, all of the $n = 2$ species we have studied for different coumarins show an affinity for the >C=O group in the electronic ground state. Such structural differences between subtly different coumarin molecules and different numbers of clustering species challenge the current predictive capacity of molecular structure calculations, and bond-specific analysis is required, of the type provided by infrared double-resonance techniques.

3.3. *Excited-state infrared spectra of C151-based clusters*

3.3.1. *The water dimer cluster C151/$(H_2O)_2$*

The excited-state infrared spectrum of C151/$(H_2O)_2$ for different excitation conditions was recently

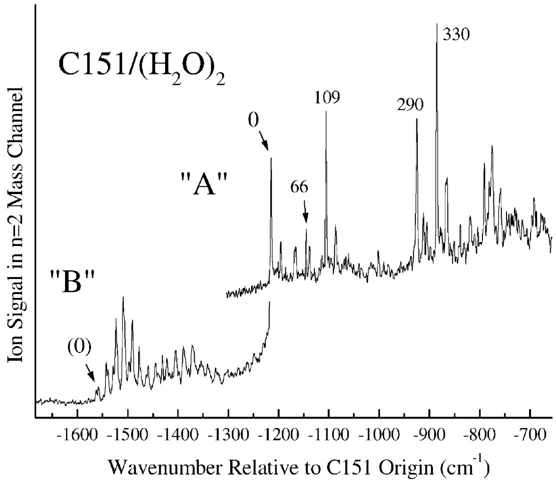
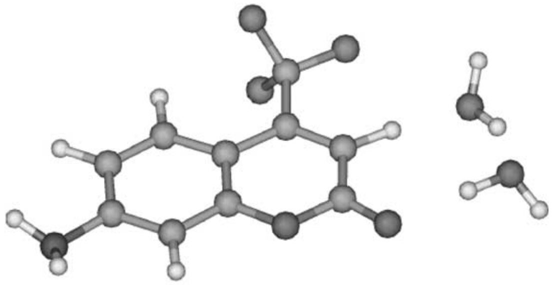


Fig. 8. Mass-resolved excitation spectrum showing the two conformers of C151/$(H_2O)_2$. The signal from the dominant “A” conformer is roughly 10× stronger than that from “B.” Originally presented in [53].

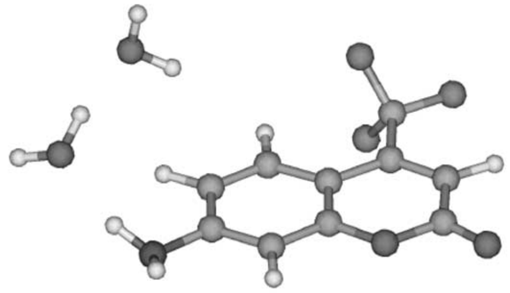
published [53]. An important property of this cluster is the presence of two distinct conformers in the electronic ground state, which are indicated in the mass-resolved excitation spectrum shown in Fig. 8. The “A” form has a red shift of 1214 cm^{-1} from the C151 origin, and has a relatively simple spectrum, whereas the “B” form (shift ≈ 1560 cm^{-1}) reveals a long progression in a mode near 10 cm^{-1}. The latter behavior is characteristic of clusters attached via a donor NH···O hydrogen bond to C151 [52]. Fig. 9 shows calculated structures considered to represent the “A” and “B” forms, resulting from a combination of semiempirical (PM3) and DFT calculations. The “A” structure shown here represents a refinement from [53], based on more detailed DFT calculations, which allow for the acidity of the CH proton adjacent to the >C=O group. However, the actual hydrogen-bond coordination geometry at the >C=O group is not known.

Fig. 10 shows a sequence of infrared spectra generated by double-resonance experiments on C151/$(H_2O)_2$. These results were published in [53]. The bottom spectrum, due to the ground state of the “A” conformer, shows a doublet at 3721/3726 cm^{-1}, which is attributed to stretch modes of non-hydrogen-bonded OH groups. These are substantially decoupled from their hydrogen-bonded OH counterparts at 3477 and 3510 cm^{-1}. The two narrower, weaker bands at 3455 and 3554 cm^{-1} can be assigned by comparison with bare C151 to the unperturbed symmetric and antisymmetric vibrations, respectively, of the NH_2 group. Like the case of C151/CH_3CN in Fig. 6, this observation shows that the water dimer is not bound at the –NH_2 group of the coumarin molecule. It is important to note that the same ground-state infrared spectrum was observed, independently of which resonance of the “A” conformer was probed. This confirmed the original assignment that only one species is responsible for the resonances to higher energy than the origin of the “A” conformer [26].

The two “A*” spectra in Fig. 10 result from bringing the resonant pulse in before the infrared pulse.



Conformer "A"



Conformer "B"

Fig. 9. Calculated structures of the “A” and “B” conformers of C151/$(H_2O)_2$, based on a combination of semiempirical and DFT calculations. The assignments were made via infrared spectroscopy.

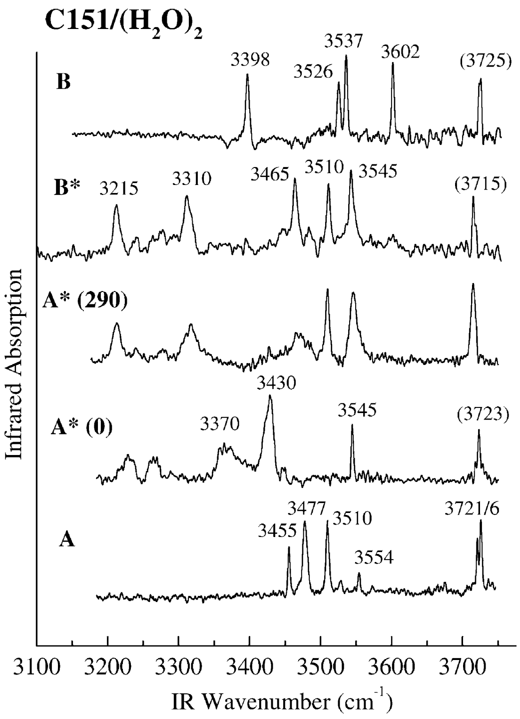


Fig. 10. Infrared spectra of the "A" and "B" conformers of C151/$(H_2O)_2$ for different excitation conditions.

Following electronic-origin excitation (A*(0)), infrared irradiation within the first few nanoseconds catches the system in the metastable excited "A" structure, showing a radical difference in the infrared spectrum from the ground state. Specifically, this spectrum reveals bands at 3430 and 3545 cm^{-1}, which strongly resemble the bands of bare C151, C151/$(H_2O)_1$ ("A" conformer) and C151/$(CH_3CN)_1$ in location, relative width and relative intensity [27] (see Figs. 4 and 6). We confidently assign these to the antisymmetric and symmetric stretch combinations of the NH_2 group in the S_1 state. Notably, this spectrum also shows a large downshift in the frequencies of the hydrogen-bonded OH-stretch modes, which appeared in the ground state at 3477 and 3510 cm^{-1}. In the excited state, there is a diffuse band near 3370 cm^{-1} and two smaller bands near 3250 cm^{-1}, none of which is evident in the ground-state spectrum. For comparison, the spectrum of excited C120/$(H_2O)_2$ gives rise to a band near 3360 cm^{-1}. We note in parenthesis that jet cooling conditions needed to be carefully optimized so as to stabilize the zero-point excited "A" form of the C151 cluster. This behavior is consistent with the low barrier (60 cm^{-1}) for conformational relaxation [26].

The result of vibronically exciting the "A" species is seen from the +290 cm^{-1} vibronic level (A*(290) in Fig. 10). Notably, all principal resonances have shifted from the case of pure electronic excitation (A*(0)). This result is different from simple IVR, which tends to broaden, but not displace the infrared resonances, and implies that a structural change has occurred. Thus, excess vibrational energy causes loss of the 3430 cm^{-1} feature, a small, but significant downshift of the free-OH resonances, a re-emergence of a 3510 cm^{-1} feature, and a broadening and strengthening of a feature at 3547 cm^{-1}. There is also a pair of broader bands at 3215 and 3310 cm^{-1}. Moreover, we can confirm that the onset of the spectral change occurred between 47 and 66 cm^{-1} excess energy, consistently with earlier fluorescence data, where the onset of a fluorescence Stokes shift was observed [26]. The very strong 3430 cm^{-1} band persisted weakly at +109 cm^{-1}, but Fig. 10 shows little contribution at +290 cm^{-1}. We note that the 3430 cm^{-1} feature is attributed to the non-hydrogen-bonded NH_2 symmetric stretch mode, suggesting that relaxation involves increased perturbation of this group. Since this strong band is nearly eliminated in the 290 cm^{-1} trace, we conclude that the residual contribution of the "A" structure to the "relaxed" cluster at this energy is quite small.

The infrared spectra characteristic of the ground and excited states of conformer "B" are shown in the upper part of Fig. 10. The ground state (top trace) shows an incompletely resolved doublet near 3725 cm^{-1}, which represents a pair of "free"-OH resonances. However, the rest of the spectrum is completely different from the other conformer. The band at 3398 cm^{-1} is evidence for a "donor-NH" resonance, similar to the ground-state infrared bands of the water ("B" conformer; 3424 cm^{-1}), methanol (3402 cm^{-1}), ethanol (3398 cm^{-1}), acetone (3387 cm^{-1}) and di-isopropylether (3364 cm^{-1}) $n = 1$ clusters of C151. A highly significant feature in the spectrum is the strong, narrow resonance at 3602 cm^{-1}, which strongly suggests that there is a hydrogen bond to the aromatic ring [49,53,92,93]. This assignment was supported in [53] by density functional calculations.

Again, electronic excitation of "B" moves most of the resonances. It is likely that 3465 and 3545 cm^{-1} represent donor-OH, and the 3510 cm^{-1} the free-NH resonance, whereas the donor-NH resonance at 3398 cm^{-1} in the ground state is replaced by a pair of bands at 3215 and 3210 cm^{-1}. The most important result from Fig. 10 is seen by comparing the electronic-origin excited "B*" conformer and the "A" species vibronically excited into the +290 cm^{-1} band. Most of the bands correspond closely in both spectra. Any differences may be due to the ≈600 cm^{-1} greater internal energy of the "A*(290)" case. We concluded on this basis that the species sampled following electronic excitation of "B" is the same as that following conformational relaxation of excited "A." That is, vibronic excitation of "A" at ≥66 cm^{-1} gives rise to conformer "B," with an internal energy ≤640 cm^{-1}.

Since the electronic spectra overlap, conceivably excitation of "A" at +290 cm^{-1} could accidentally excite "B" directly. However, we know that the ground-state infrared spectrum, obtained by monitoring the +290 cm^{-1} resonance, is the same as the "A" trace in Fig. 10. On the other hand, simply delaying the infrared pulse behind the UV pulse for the same excitation conditions gave a spectrum dominated by conformer "B." Second, since the +290 cm^{-1} resonance is one of the stronger bands in the spectrum of the "A" conformer, this could not be confused with vibronic resonances of "B," which exhibit complex low-frequency mode progressions. Third, excitation of "A" via resonances 47, 66, and 109 cm^{-1} above the origin (not shown) showed a steady loss of the very strong 3430 cm^{-1} band (NH_2 symmetric stretch) with increasing energy. The narrow 3510 cm^{-1} band, which most likely represents the decoupled free-NH mode, also appears above 66 cm^{-1} internal energy. Also, we note that picosecond time-resolved fluorescence measurements have already shown the existence of a relaxation process for these same resonances, the measurable rate of which increases with excitation energy [26].

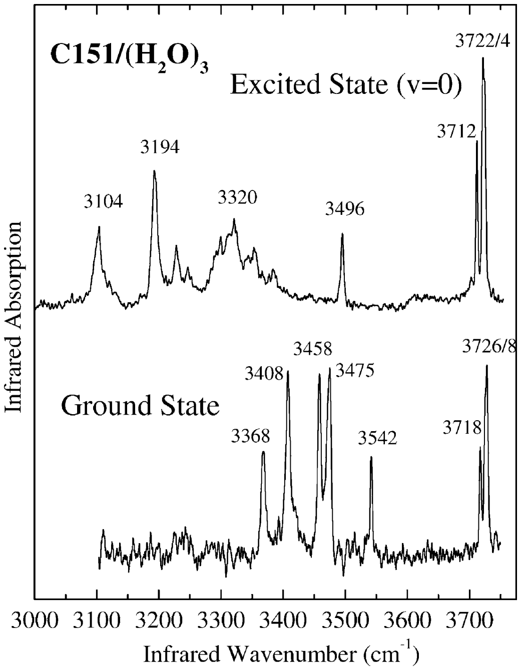


Fig. 11. Ground and excited-state infrared spectra for the water trimer cluster of C151.

Finally, we may rule out any possible confusion with the $n = 3$ cluster, which has an electronic origin ≈1350 cm^{-1} to lower energy than $n = 2$ "A" origin. This is a consideration, since predissociation of $n = 3$ clusters can generate background signal in the $n = 2$ channel. However, as Fig. 11 shows, the ground-state infrared spectrum of the $n = 3$ cluster, C151/(H_2O)$_3$, exhibits five strong resonances between 3350 and 3550 cm^{-1}, in addition to a characteristic pattern of three "free-OH" bands near 3720 cm^{-1}. In the $n = 3$ excited state, there is a prominent band at 3496 cm^{-1} and strong bands at 3104 and 3194 cm^{-1}, none of which appears in any of the spectra attributed to the $n = 2$ cluster. In passing, we note that the water trimer cluster of C151 shows a pronounced decrease in the energy of all hydrogen-bonded resonances in the excited state, to an even greater extent than the

$n = 2$ species. On the other hand, we detected no evidence of vibronically-induced conformational relaxation in this cluster, which appears to bridge the NH_2 and >C=O groups in the ground state. Incidentally, the improved signal-to-noise ratio of the electronically excited spectrum results from efficient infrared-induced fragmentation of the cluster—the upper trace in Fig. 11 was recorded via the product $n = 2$ channel, but with the resonant ultraviolet pulse tuned to $n = 3$ resonances.

3.3.2. C120/$(H_2O)_2$

For C120, the water dimer cluster shows evidence of being attached via the >C=O group, because the excited-state NH_2 stretch bands at 3436 and 3554 cm^{-1} have almost the same frequency and intensity ratio as isolated C120 (3444 and 3554 cm^{-1}). In the ground state (see Fig. 12), the "donor"-OH bands are further downshifted than in the C151 case, so that the NH_2 symmetric stretch band near 3447 cm^{-1} is presumably hidden under the stronger, broadened donor-OH resonance at 3453 cm^{-1}. However, the antisymmetric NH_2 stretch band (3549 cm^{-1}) falls near the position in the isolated C120 molecule (3543 cm^{-1}).

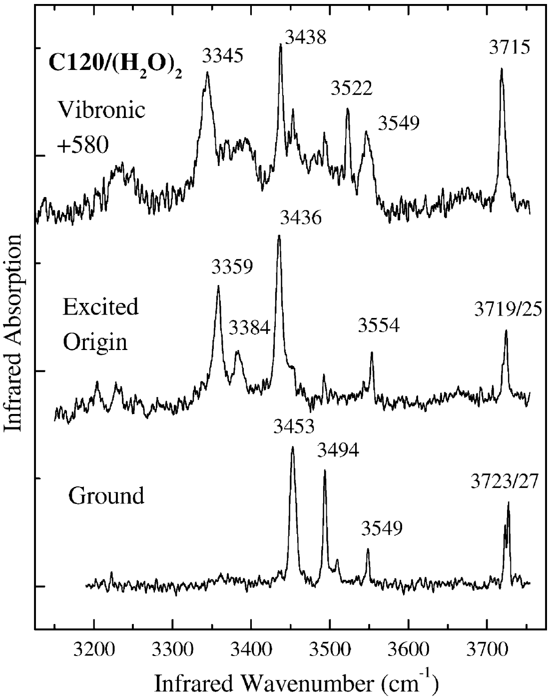


Fig. 12. Infrared spectra similar to Fig. 10, for C120/$(H_2O)_2$, showing evidence for vibronically-induced structure relaxation.

In the excited state, following excitation via the electronic-origin transition, one finds the strong OH bands to have shifted down to <3400 cm^{-1}. This again resembles behavior of C151/$(H_2O)_2$, which shows a broad band near 3370 cm^{-1}. The absence of strong resonances in the range 3440–3550, between the symmetric and antisymmetric stretch NH resonances is particularly striking in both cases. We conclude from this that the two structures are similar, and that in the excited state of the "A" conformer, the OH stretch resonances are well downshifted.

Upon vibronic excitation, the water dimer cluster of C120 develops extra features. Thus, there is a new feature at 3522 cm^{-1} and a broader feature at 3549, which is close to the trend observed in Fig. 10 for the C151/$(H_2O)_2$ case (3510 and 3547 cm^{-1}). There is also a strong feature at 3345 cm^{-1} for the C120 case, which appears to reflect the 3320 cm^{-1} feature of C151. However, although there is a weak feature near 3220 cm^{-1} for the C120 case, this cannot be assigned with confidence at this stage. Finally, similarly to C151/$(H_2O)_2$, the C120 cluster shows an intensification, broadening and slight downshift of the "free"-OH band(s) near 3715 cm^{-1}. We conclude that this cluster is relaxing similarly to the C151 case, so that the product state may involve the excited "B" conformer. In the C120 case, though, the persistence of the resonance near 3438 cm^{-1} suggests that the relaxation is not complete, as this is most likely evidence for the strong, unperturbed NH_2 symmetric stretch resonance. We conclude from this work that C120/$(H_2O)_2$ behaves similarly to the C151 case, although showing less complete conformational relaxation. This behavior appears consistent with literature data, which show that the spectral shift of C120 in solution is less than for C151 in corresponding solvents [5]. This is attributed to a smaller dipole moment change upon electronic excitation of C120.

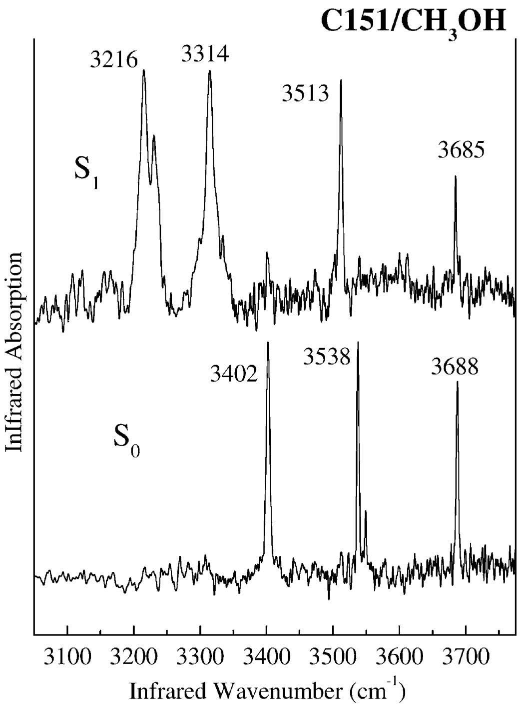
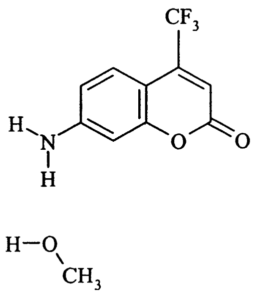


Fig. 13. Infrared spectra of the water trimer cluster of C151 in the ground and excited states, showing the development of an additional resonance in the excited state.

3.3.3. Other clusters attached via the NH_2 group

One significant difference between the electronically excited “A” and “B” sites for hydrogen-bonded clusters of C151 is the appearance of pairs of prominent, broadened infrared resonances in the range 3100–3350 cm^{-1}. Fig. 13 shows the specific case of C151/CH_3OH, comparing the ground- and excited-state infrared spectra. There are three high-energy fundamentals in the range 3350–3700 cm^{-1}, namely the OH stretch of methanol and the two NH-stretch modes of C151. The 3688 cm^{-1} feature in the lower spectrum is almost at the same position as the natural OH-stretch resonance of free-methanol, whereas the 3402 and 3538 cm^{-1} bands provide evidence for “donor”- and “free”-NH stretch resonances, respectively. This spectrum is clear evidence for the attachment of the methanol molecule to C151 via a hydrogen bond of the type NH$\cdots$O, as indicated in the diagram. In the excited-state spectrum, the “free”-OH resonance is evident at 3685 cm^{-1}, and the band at 3513 cm^{-1} is readily assignable to the “free”-NH mode. However, the two strong bands at lower energy are seen in place of the single ground-state “donor”-NH band



The appearance of these two lower-energy bands is revealed by Fig. 14 to be a common property of all electronically excited clusters of C151 having an NH$\cdots$O hydrogen bond. These include the $n = 1$

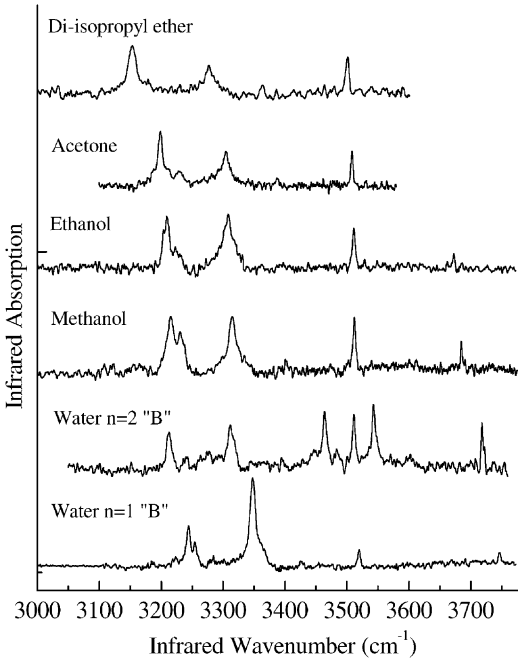
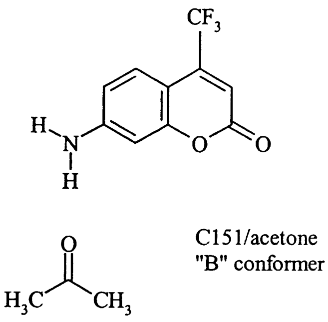


Fig. 14. Excited-state infrared spectra for a group of clusters known to attach to C151 via a hydrogen bond of the type NH$\cdots$O. Each spectrum shows a pair of prominent, broadened low-energy resonances.

cluster with water (“B” conformer; 3237, 3346 cm^{-1}), $n = 2$ cluster with water (“B” conformer; 3215, 3310 cm^{-1}), and the $n = 1$ clusters with methanol (3215, 3315 cm^{-1}), ethanol (3209, 3308 cm^{-1}), acetone (3200, 3306 cm^{-1}) and di-isopropyl ether (3153, 3277 cm^{-1}). Even the water trimer cluster (Fig. 11) shows a pair of strong resonances at 3104 and 3194 cm^{-1}. We note that, for the $n = 1$ clusters going from bottom to top in Fig. 14, there is a correlation between the increasing strength of the interaction, measured either by the excitation red shift (690–995 cm^{-1}) or the red shift of the low-energy infrared resonances, and the increasing base strength of the complexing molecule.

3.3.4. C151/acetone

The acetone cluster of C151 represents an important counterpart of the cluster C151/$(H_2O)_2$, in two important respects. First, two conformers are evident from the excitation spectrum shown in Fig. 15. Like the water dimer case, the longer-wavelength component (red shift 995 cm^{-1}; denoted “B”) shows an active low-frequency mode progression in $\approx$10 cm^{-1}, and in this case the “B” species appears to be in the majority. At -597 cm^{-1}, there is the onset of another spectrum (denoted conformer “A”), which is distinguished by the absence of a low-frequency mode progression. This spectrum is, however, underlaid by a strong signal arising from higher-energy components of the “B” spectrum.



C151/acetone
"B" conformer

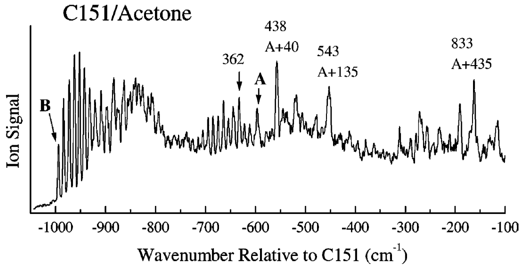


Fig. 15. Mass-resolved excitation spectrum of C151/acetone, monitored via the $n = 1$ channel. Two conformers are indicated, having red shifts 597 cm^{-1} (A) and 995 cm^{-1} (B).

The ground-state infrared spectrum of the “A” conformer (Fig. 16) shows clear features at 3453 and 3554 cm^{-1}, which lie close to the positions for C151 itself. This confirms that the NH_2 group is relatively unperturbed. As the figure shows, there is an overlapping component from the “B” conformer, for which the resonances at 3387 and 3531 cm^{-1} show a perturbation of the NH_2 group.

In the excited state, the two ground-state resonances of the “B” conformer are replaced by three resonances,

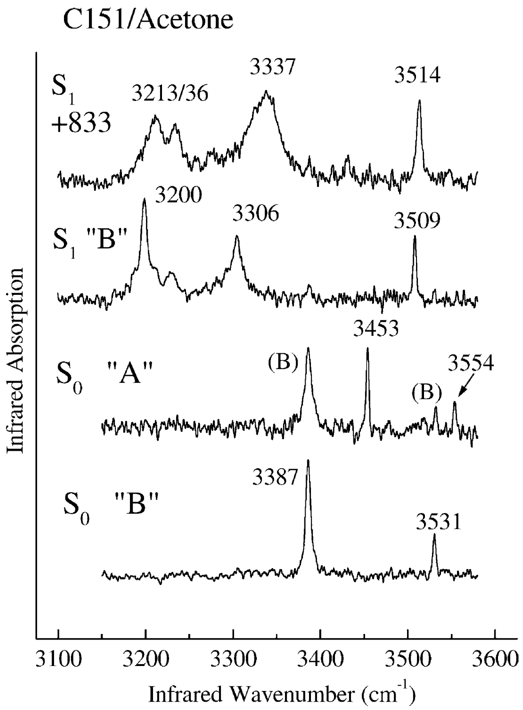


Fig. 16. Ground and excited-state infrared spectra of C151/acetone for four different excitation conditions. The resonances are labeled in Fig. 15.

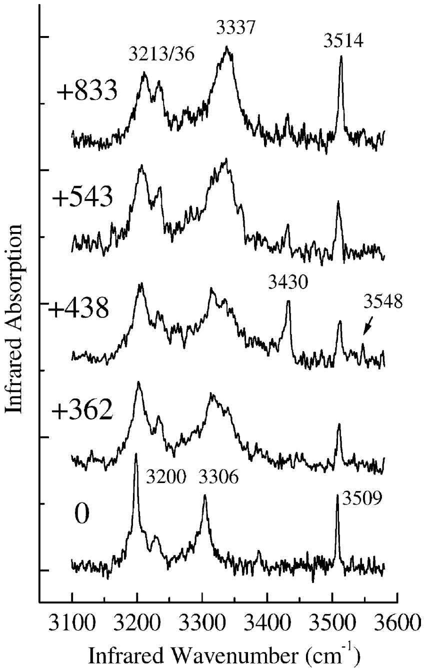


Fig. 17. Same as Fig. 16, except for the excited state as a function of excitation energy. Resonances indicated are shown in Fig. 15.

including a narrow 3509 cm^{-1} band, assigned to the "free"-NH bond. The two strong resonances at lower energy, spaced by $\approx$100 cm^{-1}, follow the pattern established for several other clusters in Fig. 14. Upon excitation at higher internal energy, the lower two resonances broaden and shift to higher energy, which may suggest increased non-radiative coupling and weakening of the hydrogen bond. We also note the presence of a shoulder at 3236 cm^{-1}, which may be due to Fermi resonance. To examine the trend more closely, Fig. 17 shows a sequence of infrared spectra for the electronically excited acetone cluster, all resulting from excitation via prominent resonances of either the "A" or "B" forms (see Fig. 15). The lowest-energy excitation (0) populates the $v = 0$ level of the "B" conformer, giving the spectrum noted above, with two features in the low-energy region. At an internal energy of 362 cm^{-1}, which still excites the pure "B" species, the spectrum has evolved such that the two lower bands are much broader than at the lower energy, and their maxima have shifted up in energy. Also, the position of the "free"-NH band has shifted upwards by a small amount, although there is little increased broadening. At 438 cm^{-1}, which corresponds a transition some 40 cm^{-1} above the electronic origin of the "A" species, there is a clear resonance at 3430 cm^{-1}, with a weaker companion band at 3548 cm^{-1}, which correspond to the symmetric and antisymmetric stretch modes of the non-hydrogen-bonded NH_2 group (see Fig. 10). Features such as this are consistent with other cases noted above, and show that the structure of the "A" species persists close to the electronic origin. As the internal energy is raised further above the origin of the "A" species, although the excitation is always into prominent vibronic bands of "A," the contribution from the 3430 cm^{-1} band is much reduced. This implies that the NH_2 group is becoming hydrogen-bonded in the excited state. We have confirmed this by comparing the ground-state infrared spectra for different vibronic bands, finding in all cases above the "A" origin that the data reproduced the "A" spectrum ground-state shown in Fig. 16. Thus, we are satisfied that the top three traces in Fig. 17 result from excitation primarily of the "A" species. The general conclusion from these observations is that the electronically excited "A" conformer of C151/$(CH_3)_2CO$ readily converts to the "B" species via vibrational activation. In this respect, the behavior of the acetone 1:1 complex with C151 is parallel to that of the water dimer cluster with the same molecule. Both show evidence for vibrationally activated conformational change driven by electron-density redistribution in the excited state.

4. Discussion

At this stage, we do not completely understand the nature of the pairs of bands <3400 cm^{-1} for the clusters attached to C151 via NH$\cdots$O hydrogen bonds, which are clearly shown in Figs. 14 and 17. However, two primary candidates include Fermi resonance interactions and a possible proton transfer equilibrium.

First, many examples of Fermi resonance interactions have been seen, particularly in the excited-state

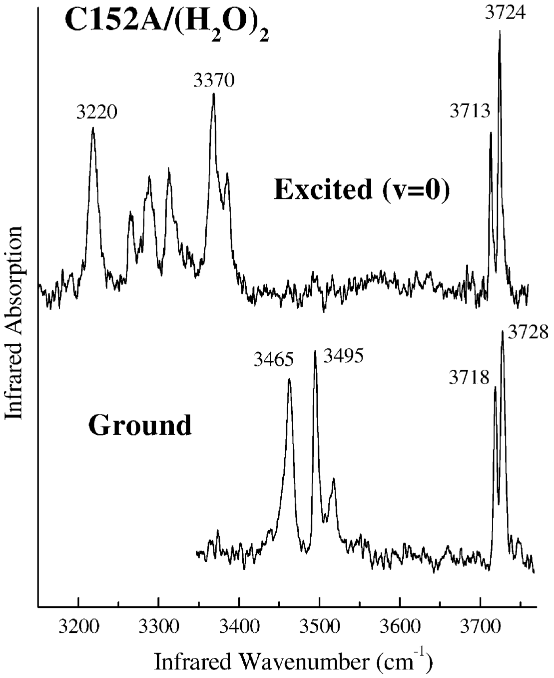


Fig. 18. Ground and excited-state infrared spectra of the water dimer cluster: C152A/$(H_2O)_2$. This shows the increased complexity in the excited state, possibly due to Fermi resonance coupling with several undetermined overtone or combination bands.

infrared spectra of molecular clusters. Indeed, considering the density of vibrational states in large-molecule clusters near 3500 cm^{-1}, it is surprising that the infrared spectra are so simple. This implies that Fermi resonance interactions are usually weak, and that the coupling of many non-hydrogen-bonded modes to the quasi-continuum is often less than the width of the rotational envelope. Such interactions can cause the appearance of multiple resonances in an electronic or vibrational spectrum, due to the interaction of a strong oscillator, such as an NH or OH stretch mode with overtones and combinations of other modes lying close in energy. One type of such interaction is commonly seen to result in broadening of resonances, such as for the donor-OH band at 3465 cm^{-1} in ground-state C152A/$(H_2O)_2$ (lower trace of Fig. 18), the excited-state symmetric-stretch mode of isolated C151 (top trace of Fig. 4) or in a more extreme case, the 3337 cm^{-1} feature in the top trace of Fig. 16 following vibronic excitation of the acetone complex. In each case here, it is likely that the promoting mode interacts with a quasi-continuous background of states, leading to ultrafast vibrational relaxation. Another case of Fermi resonance is exemplified by C152A/$(H_2O)_2$ in Fig. 18. This species, which has a similar structure to the “A” form of the cluster C151/$(H_2O)_2$ shows one sideband on the 3495 cm^{-1} donor-OH resonance, assumed due to Fermi resonance. However, in the excited state, there are at least three additional resonances. In this case, there is no evidence of structure relaxation, because the spectrum is nearly independent of internal energy. The complex excited-state vibrational spectrum appears to be due to an intermediate form of Fermi resonance coupling, where several mode combinations are intensified and presumably shifted by coupling to the two OH-donor modes. In such cases, assignment of individual resonances becomes difficult.

A third case of Fermi resonance coupling, which could be responsible for the discrete pairs of resonances observed in Figs. 10, 11, 13, 14, 16 and 17, would involve stronger coupling of the oscillator strength of an NH mode to the overtone of a single vibration. A logical candidate in the 3200–3300 cm^{-1} region would be the overtone of the bending mode of the hydrogen-bonded NH_2 group, since such a resonance is known in aniline and β-naphthylamine to occur as a weak ground-state feature near 3240 cm^{-1} [94]. In fact, reference to Figs. 13, 14 and 17 reveals evidence for such an additional feature in the spectrum. At this point it is unclear, however, whether a Fermi resonance interaction is responsible for the symmetrical pair that appears to form in many of the cases reported here, and further work is needed.

Interaction with a higher electronic state is another possibility, as we know that the NH_2 symmetric stretch mode of the uncomplexed molecule is significantly perturbed by electronic excitation. However, the strongest argument against this possibility appears to come from the acetonitrile case, where there is a large change in the electronic energy, and yet the infrared spectrum in the 3100–3600 cm^{-1} region is nearly the same as C151 itself in both the ground and excited states. Also, one would expect that the influence of a more highly excited state would become increasingly more evident to higher energy, which we do not see.

Another possibility meriting consideration is that a proton transfer equilibrium involving the NH$\cdots$O bond develops in the excited state. In this picture, the shift in electron density upon electronic excitation would increase the acidity of the NH bond relative to the more basic complexing molecule. Complete proton transfer from nitrogen to oxygen would conserve the number of infrared fundamental resonances. However, an incomplete proton transfer interaction in which NH$\cdots$O and N$\cdots$HO hydrogen bonds coexist could generate an additional strong band. One reason to favor this answer is that the effect increases significantly with increasing base strength of the attached molecule. Also, the effect is unique to the excited state, where NH protons are known be more acidic than in the ground state. This phenomenon, leading to the rearrangement of hydrogen bonds, is part of the driving force for the conformational relaxation events described above.

Also, it is significant to note that studies on the dimer of 4-aminophthalimide (4AP) generate similar groups of resonances to the case of C151/acetone. Although this is presented elsewhere [57,65], it is worth comparing the spectrum presented in Fig. 19 with, for example, the data for C151/acetone in Fig. 16, or other species in Fig. 14. The 4AP dimer, which has two NH$\cdots$O hydrogen bonds as indicated, has a simple ground-state spectrum showing free-NH (amino) (3548 cm^{-1}), free-NH (imide) (3494 cm^{-1}) and donor-NH (3426 cm^{-1}) resonances. However, in the excited state, whereas the imide free-NH stretch mode downshifts only slightly (3469 cm^{-1}), the amino NH bonds give rise to two sets of three resonances. That is, the 3426 cm^{-1} feature gives rise to four broadened, strongly red-shifted resonances, whereas the 3548 cm^{-1} feature evolves into two slightly broadened, weakly red-shifted bands. These assignments are justified elsewhere, based on the response to excess vibrational energy. For the present context, it is important to note that the two NH$\cdots$O bonds in this dimer appear to reflect the behavior of the simple coumarin clusters. Certainly, the separation into two distinct groups of three cannot be explained on the basis of Fermi resonance interactions alone, and either exciton or proton transfer arguments need also to be taken into account.

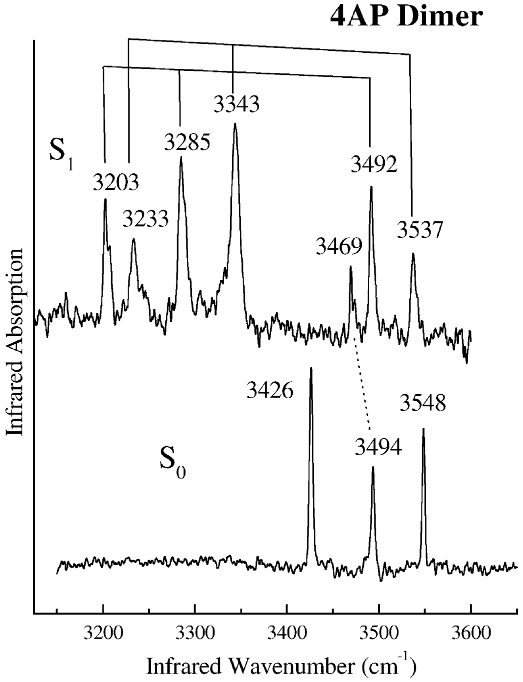
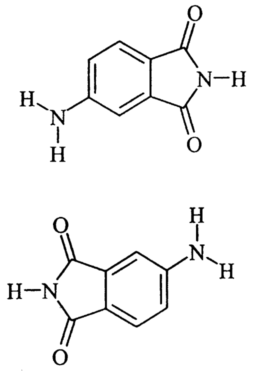


Fig. 19. Ground and excited-state infrared spectra of the 4AP-dimer cluster. This shows a special case of increased complexity in the excited-state spectrum, where the number of resonances expands from three to seven.



4AP Dimer

At this point, it is unclear what is responsible for the presence of the extra bands in these spectra, further evidence is being sought through experiments. One type of experiment currently in progress involves Coumarin 500, in which one proton of the NH_2 group in C151 is replaced by an ethyl group. This may be able to distinguish between the proposed proton transfer and Fermi resonance mechanisms.

5. Conclusion

This work has explored the behavior of small, jet-cooled hydrogen-bonded clusters involving molecules that are commonly used in the condensed phase as solvation probes. Cluster conditions permit analysis of the consequences of electronic excitation in considerable detail, via infrared-optical double-resonance spectroscopy. The focus of the attention has been to analyze the response of different cluster structures to electronic excitation, some cases allowing comparison of different conformers of the same cluster. In three different cases, including water dimer clusters of C120 and C151 and the acetone 1:1 cluster with C151, infrared evidence shows that there is a structural relaxation. In all three cases, the end result of the relaxation process was the formation of a strong donor hydrogen bond of the type $NH\cdots O$ from the aromatic NH_2 group. Further analysis of the infrared spectra for C151 clusters involving this type of hydrogen bond has revealed a strong pair of resonances in the low-energy range ($3100–3350\,cm^{-1}$), spaced by $\approx 100\,cm^{-1}$. These apparently replace the single “donor”-NH resonance of the ground state. Comparison with recently studied doubly hydrogen-bonded dimers of aminophthalimide derivatives, which also undergo large changes in dipole moment upon excitation, has suggested that the additional strong resonance results from a proton transfer equilibrium. This involves a rapid exchange between hydrogen bonds of the types $NH\cdots O$ and $N\cdots HO$. Further evidence for this possible mechanism will be sought through a combination of (a) extension of the infrared spectrum to the $>C=O$ fundamental frequency to study the consequences of hydrogen bonding on that group and (b) direct analysis via ultrafast measurements designed to time-resolve the evolution of the infrared spectrum, and (c) the use of secondary amino coumarins instead of primary amines C151 and C120, to modify the relationship between NH-stretch and bend modes.

Acknowledgements

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