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Strong Experimental Evidence of C−H···O Hydrogen Bonds in Cyclopentanone: The Splitting of the ν(C=O) Mode Revisited

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The assignment of the splitting of the ν(C=O) mode in cyclopentanone is reassessed through an extensive vibrational study, including temperature and solvent variation studies, isotopic substitution, and ab initio calculations of monomer and dimer structures and spectra. The results show that the assignment of the splitting of the ν(C=O) mode to Fermi resonance is based on several of erroneous observations, and present strong experimental evidence of molecular association through C−H···O hydrogen bonding.

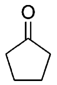
Introduction

C−H···O hydrogen bonds have attracted considerable interest over the past few years. The questions on the nature and nonconventional properties of this kind of hydrogen bonding are the subject of some controversy.[1−11] In particular, several ab initio theoretical studies have been published aiming at the understanding of the physical basis of the interaction.[3−8] In what concerns the experimental studies, some attention has been given to the spectroscopic manifestations of the C−H···O bonding.[9−17] Given the weakness of the interaction (typically below 8 kJ mol^{-1}),[2,14−17] its effects can easily be obscured by stronger effects or even assigned to better known phenomena.

Cyclopentanone (CP, Chart 1) is a particularly interesting molecule in this context: the vibrational spectra of solid and liquid CP present two bands in the region of the carbonyl stretching mode (ν(C=O)), whereas a single one is observed in the gas-phase spectrum. This splitting of the ν(C=O) mode in the condensed phases was first assigned to C−H···O hydrogen bonds by Suetaka, back in 1952.[18] Suetaka's explanation was generally refuted, not only because "the experience has never revealed strong hydrogen bonding between a carbonyl group and a methylene group"[19] but also by the erroneous observations of negligible temperature and dilution effects on the relative intensities of the ν(C=O) band pair.[20] Among the several alternative explanations proposed in the following decade (e.g., dipolar association,[21] conformational equilibrium,[19] keto−enol isomerization[22]), Fermi resonance became the most accepted one. To this consensus largely contributed the isotopic substitution studies of Jones et al.,[23−25] showing the "removal of degeneracy" due to isotopic shifts. However, it was recognized by the authors that the origin of Fermi resonance in CP is not easy to identify, and it would be necessary to assume a large anharmonicity effect to place the overtone of the ring breathing vibration near the position of the "unperturbed" ν(C=O) frequency. In addition, Bertran et al. state that the solvent-dependent intensity ratio of the ν(C=O) doublet could not be described from a Fermi resonance approach.[26]

This work reports an extensive vibrational study on the splitting of the ν(C=O) mode in CP and its deuteriotopomers, reassessing the "Fermi resonance" versus "C−H···O hydrogen bonding" assignment. From the results herein reported—including temperature and solvent variation studies, isotopic substitution, and ab initio calculations of monomer and dimer structures and spectra —molecular association through C−H···O hydrogen bonding turns out to be the most reasonable explanation for the observed splitting.

CHART 1: Schematic Representation of Cyclopentanone



Results and Discussion

Ab Initio Calculations. Although the presence of a conformational equilibrium has been suggested to justify the splitting of the ν(C=O) mode,[19] it is clear that CP has a single minimum energy structure, with C_2 symmetry (symmetry axis through the C=O bond). C_s (envelope-like) and C_{2v} (planar) structures were found to be first- and second-order saddle points, respectively.

Figure 1 shows the optimized geometry for the dimer configurations found at both the B3LYP/6-31G* and MP2/6-31G** levels, and Table 1 collects the corresponding hydrogen bonding energies. Two interesting features concerning the most stable dimer forms arise from Table 1. First, the structures of forms I and II correspond to the C−H···O-bonded structure originally proposed by Suetaka.[18] Second, the dipolar alignment dimer proposed by Baker[21] (form III) is also stabilized by C−H···O hydrogen bonds.

The dimerization energies shown in Table 1 are within the range of values reported for similar interactions.[14−17] The most stable forms are those presenting two C−H···O contacts, but because the energetic (enthalpic) factor is not that unique to be considered in the dimerization process, single bonded dimer forms (such as IV and V) are expected to have some contribution in the liquid phase. Considering the maximum ZPVE correction for dimer forms I−III (calculated at the BSSE uncorrected surface) of ca.. 3.0 kJ mol^{-1}, the resulting dimerization energy is predicted to be in the range of ca. 9−14 and ca. 5−8 kJ mol^{-1} at MP2/6-31G** and B3LYP/6-31G*, respectively.

ν(C=O) Region of the Pure Liquid at Room Temperature. The vibrational spectra of CP in the ν(C=O) region (pure liquid, room temperature) is shown in Figure 2, together with a simulation from ab initio wavenumbers. The simulation is

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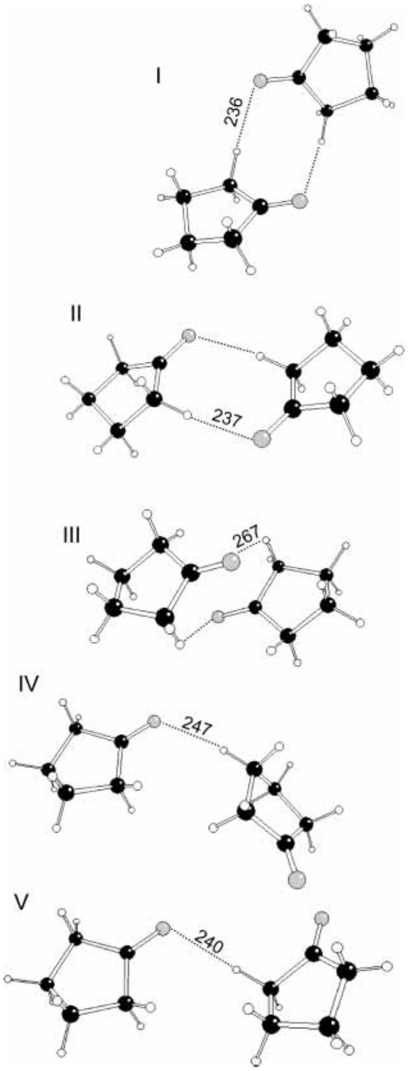

Figure 1. MP2/6-31G** optimized geometries of five low-energy dimers of cyclopentanone. Hydrogen bond distances are given in pm; the calculated dimerization energies for each dimer are listed in Table 1.

TABLE 1: Dimerization Energies (Dimer = 2 × Monomer) for Cyclopentanone Dimers (ΔE/kJ mol^{-1})

	dimer[a]				
	I	II	III	IV	V[b]
MP2/6-31G**	−26.0	−24.2	−37.0	−13.2	−11.0
after CP	−11.9	−11.1	−16.8	−5.2	−2.9
B3LYP/6-31G*	−21.1	−19.6	−21.6	−8.5	−6.3
after CP	−9.6	−8.9	−7.7	−2.6	−0.9

[a] Dimers numbered in accordance with Figure 1. CP = counterpoise correction. Absolute energy of dimer II is −541.148563 Eh (B3LYP/6-31G*) and −539.502706 (MP2/6-31G**). [b] Saddle point (one imaginary frequency).

obtained from a 60:40 mixture of monomer and dimer III, using scaled wavenumbers and Gaussian band profiles with 18 cm^{-1} width, and illustrates the predicted effect of the dimerization (other combinations of monomer plus dimer forms can be used to reproduce the same band profile).

The band maxima occur at ca. 1728 and ca. 1744 cm^{-1}, respectively. The intensity ratio *r*, defined as $I(1728)/I(1744)$, has nearly the same value ($r = 0.54$ and 0.52) for both infrared and Raman spectra, a condition required for a Fermi resonance situation (because *r* is determined by the coupling coefficient *W*) but that can also occur for a dimerization process. More interesting is the measurement of the depolarization ratio for these bands: as can be seen from Figure 2, *r* changes from I_{VV} to I_{VH} spectra, meaning that the two band components are different in nature.

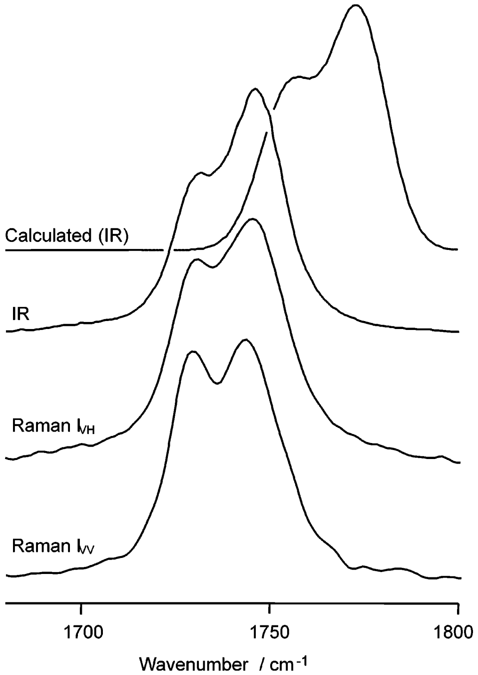

Figure 2. Vibrational spectra of liquid cyclopentanone at room temperature in the region of the C=O stretching modes. From bottom to top: Raman I_{VV} spectrum, Raman I_{VH} spectrum, FT-IR spectrum, and calculated IR spectrum for a mixture of monomer and dimer form III.

Temperature Effects. Temperature effects provide the first strong evidence against Fermi resonance. Previous studies have described the temperature effects as negligible (and opposing the expected behavior of *r* for a dimerization equilibrium).[20] However, as can be seen from Figure 3, the intensity ratio of the 1728/1744 ν(C=O) band pair is strongly temperature-dependent. Within the 223−358 K temperature range, *r* decreases from 1.1 to 0.3 with increasing temperature, showing an intensity inversion at fixed wavenumbers, quite unexpected for a Fermi resonance case. In fact, to describe the effect within the Fermi resonance approach, it is necessary to assume a large dependence of the coupling coefficient *W* with temperature and the simultaneous shift of the "unperturbed" overtone and fundamental levels, with inversion of their relative positions. Figure 4 shows the temperature dependence of the hypothetical *W* value and "unperturbed" levels required for a Fermi resonance assignment, stressing the oddities of such an assignment.

A much easier explanation to the temperature effects in the ν(C=O) band pair (shown in Figure 3) is obtained by assuming the presence of a C−H···O dimerization equilibrium. The temperature increase leads to a decrease of dimer forms, and consequently the 1728 cm^{-1} band (assigned to the hydrogen-bonded carbonyl groups) loses intensity to the 1744 cm^{-1} band (assigned to the free carbonyl groups). A logarithmic plot of the intensity ratio *r* against reciprocal temperature yields a value of $\Delta H = 5.8 \pm 0.6$ kJ mol^{-1} for the dimerization process. This value is within the range of reported values for C−H···O dimerization equilibria[14−17,27,28] and in agreement with the values obtained from ab initio calculations.

Solvent Effects. The 1728/1744 intensity ratio *r* is also strongly affected by dilution, in clear contradiction with the previous report of Allen et al.,[20] as shown in Figure 5. The

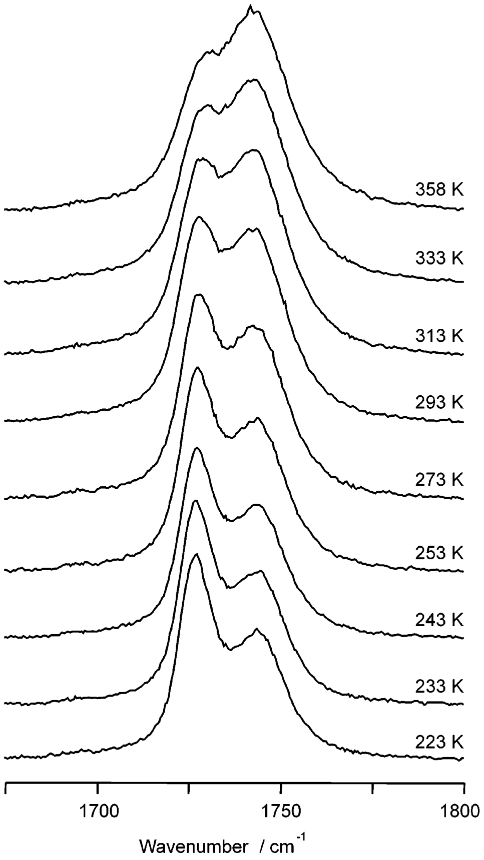

Figure 3. Raman spectra of pure cyclopentanone at several temperatures, in the region of the C=O stretching modes.

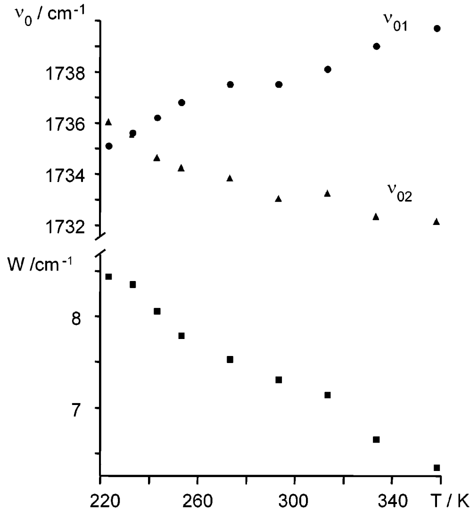

Figure 4. Temperature dependence of the parameters (*W* coefficient and "unperturbed" wavenumbers) required to describe the hypothetical Fermi resonance involving the C=O stretching modes.

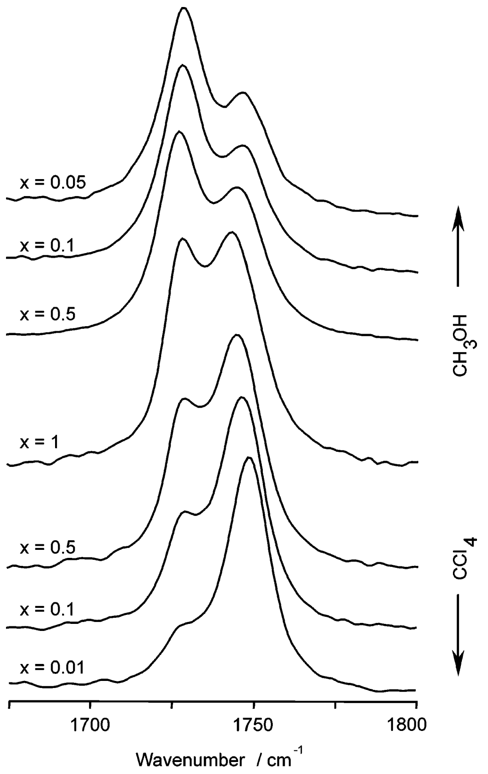

Figure 5. Raman spectra of several cyclopentanone solutions in the region of the C=O stretching modes: top, methanol solutions; middle, pure liquid; bottom, CCl_4 solutions.

dilution with hydrogen-bonding donor solvents, such as methanol, results in the progressive enhancement of the "hydrogen-bonded carbonyl" 1728 cm^{-1} band (Figure 5, top half). On the other hand, dilution with nondonor solvents always causes an intensity increase of the "free carbonyl" 1744 cm^{-1} band, regardless of solvent polarity (e.g., $C_6H_4Cl_2$, $\epsilon = 10.9$; CCl_3NO_2, $\epsilon = 7.3$; CCl_4, $\epsilon = 2.0$). This effect is shown in Figure 5, bottom half, for CCl_4 solutions. On the whole, Figure 5 can be read, from bottom to top, as the result of the increase of the ratio "number of hydrogen-bonding donors/number of carbonyl groups", and gives additional support to the assignment of the 1744 and 1728 cm^{-1} bands to the free and bonded ν(C=O) modes, respectively.

Isotopic Substitution. Isotopic substitution is widely used to identify Fermi resonance doublets, as isotopic shifts often remove the accidental degeneracy, or near-degeneracy, that originates the resonance. In the case of CP, full and partial deuteration, as well as ^{16}O to ^{18}O substitution, were claimed to yield a single ν(C=O) band,[23−25] thus supporting the Fermi resonance interpretation of the splitting of the ν(C=O) mode in bare CP. However, the careful observation of the published spectra raised some doubts on this assertions, and new vibrational spectra have been recorded.

Figure 6 shows the Raman spectra of the isotopic forms CP-d_8, CP-α-d_4, and CP-β-d_4 (pure and diluted) in the region of the ν(C=O) mode. As can be seen, it is possible to identify two bands in this region for all the isotopomers studied (although for pure CP-β-d_4 the presence of two bands is mainly inferred from the large width and asymmetry of the band profile). More convincing is the effect of dilution in CCl_4: in all cases, the dilution leads to an intensity increase of the higher wavenumber "free carbonyl" band.

The separation between the free and bonded ν(C=O) modes for CP-h_8, CP-d_8, and CP-α-d_4, is 16, 10, and 12 cm^{-1}, respectively. For CP-β-d_4, the best two-band fit is obtained for a "free"-"bonded" band separation of ca. 9 cm^{-1}.

C—H Modes. The presence of C—H···O hydrogen bonds in CP is expected to be also revealed by frequency shifts of the modes involving the C—H oscillator. Ab initio calculations predict a frequency increase (blue shift) upon C—H···O dimerization for the C—H bending (β(C—H)) modes, ranging from +5 to +14 cm^{-1}. In what concerns the C—H stretching (ν(C—H)) modes, both red (ca. −2 cm^{-1}) and blue (up to +20 cm^{-1}) shifts are predicted, depending on the dimer form. Although the increase of the β(C—H) force constant is a typical effect of hydrogen bonding, the blue shift of the ν(C—H) mode

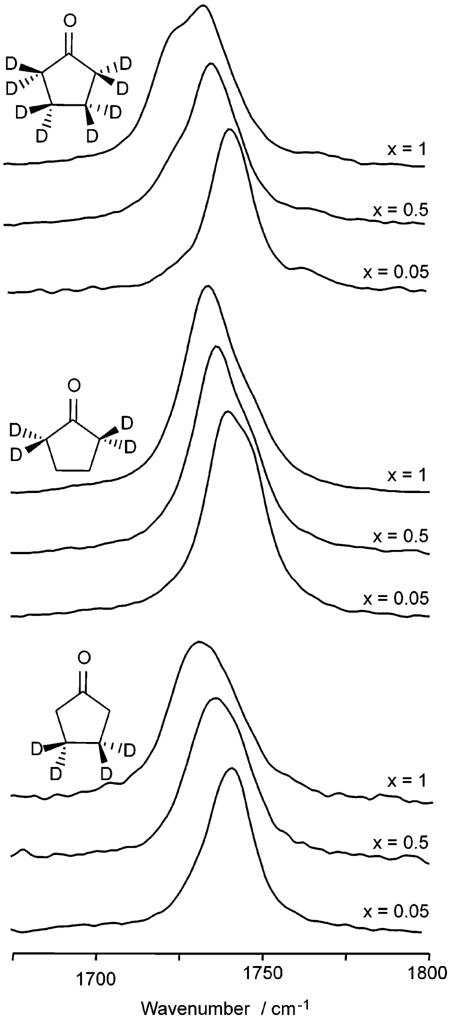

Figure 6. Raman spectra of cyclopentanone isotopomers in the region of the C═O stretching modes, for pure liquids and CCl_4 solutions: cyclopentanone-d_8, cyclopentanone-α-d_4, cyclopentanone-β-d_4.

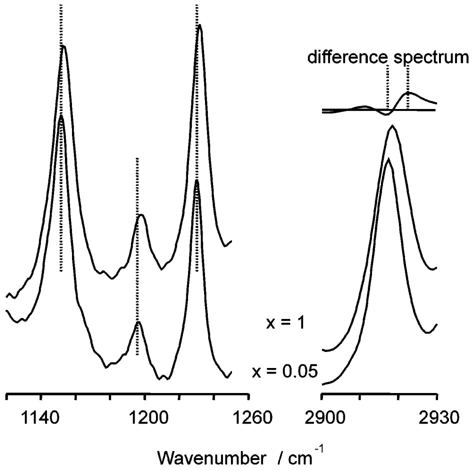

Figure 7. Effect of dilution (in CCl_4) on the (left) C—H bending modes of cyclopentanone and (right) C—H stretching mode of cyclopentanone-α-d_4 (difference spectrum (pure-diluted) is shown).

is a peculiar feature of some $C-H\cdots O$ contacts,[3-5,29] whose experimental observation is not straightforward.

Blue shifts with increasing concentration (i.e., with increasing $C-H\cdots O$ contacts) are observed for the β(C—H) modes of CP and of both CP-d_4, in CCl_4 solutions (Figure 7a). The shifts are observed for several bending modes and range from +1 to +3 cm^{-1}. In what concerns the ν(C—H) modes, only Cp-α-d_4 displays an observable shift (ca. +2 cm^{-1}). This shift is apparent from both the movement of the band maximum and the increase of the band asymmetry (Figure 7b). Though the presence of such shifts gives additional evidence of $C-H\cdots O$ bonding, a point of caution should remain because the shifts are very small and well below the predicted ab initio values.

Experimental Section

Cyclopentanone and remaining reagents were obtained from Aldrich Co. and used without further purification. Isotopic labeled forms of cyclopentanone were synthesized as described bellow.

Raman spectra were recorded on a Jobin-Yvon T64000 spectrometer with a CCD detector, using the 514.5 nm line of an Ar^+ laser (Coherent-Inova 90) and on a FT Bruker RFS-100 spectrometer using a Nd:YAG laser (Coherent Compass-1064/500N) with excitation wavelength of 1064 nm, using 2 cm^{-1} resolution. The liquid samples were sealed in Kimax glass capillaires (i.d. ≅ 0.8 mm).

FT-IR spectra were collected on a Mattson 7000 spectrometer operating in the 400−4000 cm^{-1} range, using 1 cm^{-1} resolution.

Ab initio calculations were performed using the Gaussian 98W program package, rev. A11.[30] Molecular structures were fully optimized at the B3LYP/6-31G* and MP2/6-31G** standard levels. The basis set superposition error (BSSE) correction for the dimerization energies has been estimated by counterpoise calculations using the MASSAGE option of Gaussian 98W. Harmonic vibrational wavenumbers were calculated at the B3LYP/6-31G* level and scaled by the standard factor of 0.96.[31]

Synthesis of Cyclopentanone-α-*d*$_4$ and Cyclopentanone-β-*d*$_4$. Commercial cyclopentanone (20 mL, 0.23 mol) was stirred with anhydrous Na_2CO_3 (0.5 g, 4.5×10^{-3} mol) and D_2O (42 mL, 2.3 mol) for 24 h, at room temperature, under N_2 atmosphere and in the dark. The deuterated cyclopentanone was extracted with dichloromethane (4 × 25 mL) and dried with anhydrous sodium sulfate overnight. After filtration, the solution was evaporated with caution due to volatility of cyclopentanone. The procedure was repeated to ensure maximum exchange percentage (≈95% as determined by ^1H NMR). To obtain cyclopentanone-β-d_4, the same procedure was repeated using CP-d_8 and H_2O.

Synthesis of Cyclopentanone-*d*$_8$. Adipic-d_8 acid-d_2 (5 g, 3.2×10^{-2} mol) was mixed with deuterated barium hydroxide (0.25 g, 1.1×10^{-3} mol) (prepared by mixing barium oxide with D_2O and drying under vacuum) in a round-bottom flask with a magnetic stirrer. The mixture was distilled under a N_2 atmosphere at 280−290 °C. The distilled product was cooled with ice to prevent volatilization and washed with a saturated solution of K_2CO_3 in D_2O, followed by D_2O, and finally dried with anhydrous sodium sulfate overnight. After filtration, CP-d_8 was obtained with 50% yield.

Conclusions

The experimental results herein reported show that the assignment of the splitting of the ν(C═O) mode to Fermi resonance is based on several erroneous observations, (mainly arising from the low quality of the vibrational spectra). The data now available allow several important observations and conclusions:

The intensity ratio of the band pair is strongly temperature dependent, ranging smoothly from 1.1 at 223 K to 0.3 at 358 K.

The intensity ratio of the band pair is sensitive to the proton donor ability of the solvent and almost insensitive to the solvent dielectric constant. Dilution in proton donor solvents (e.g., water, methanol) leads to the increase of the low-wavenumber band, whereas dilution in nondonor solvents (e.g., CCl_4, CCl_3NO_2) yields the increase of the high-wavenumber component.

The intensity ratio of the band pair is strongly dependent on the concentration. The effects described above are observed as a function of concentration and extreme r values are observed for very diluted solutions.

The isotopic H-to-D substitution, either total or partial, does not remove the splitting of the ν(C=O) mode. Both components are present in the vibrational spectra of the isotopomers studied and display the same solvent effects as bare cyclopentanone.

These effects are hardly explained in terms of Fermi resonance but match the behavior expected for an equilibrium between free and hydrogen-bonded carbonyl groups. Such equilibrium is only possible assuming the presence of C—H···O hydrogen bonds. Although some points of caution are still present, as discussed above, this work presents strong experimental evidence that the assignment of the ν(C=O) band splitting to Fermi resonance is ill-based, and the occurrence of C—H···O hydrogen bonds should alternatively be considered as a reasonable explanation. This question may look a *minor* point concerning a *small molecule*, but in view of the frequent use of the ν(C=O) mode as a vibrational probe for intermolecular interactions (and the almost ubiquity of C—H bonds in organic and biological molecules), the present work has relevant implications for the study of intra- and intermolecular interactions in carbonyl-containing systems.

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