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UV and IR photoisomerizations of an intramolecularly H-bonded molecule: acetylacetone trapped in nitrogen matrix

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Abstract

UV- and IR-induced photoisomerizations of acetylacetone trapped in a nitrogen matrix at 10 K have been carried out using a tunable (UV and IR) laser, or a mercury lamp, and have been studied by UV and FTIR spectrometries. After deposition the main form of acetylacetone is the chelated form (enol). Upon UV irradiation the intramolecular H-bond is broken, leading to non-chelated forms. These forms have been then irradiated, by a resonant $\Pi \rightarrow \Pi^*$ UV irradiation, or by resonant ν_{OH} IR irradiations. Interconversions between the non-chelated forms have been observed, providing a great amount of data for identifying acetylacetone isomers and thus for exploring intramolecular reactivity paths.

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1. Introduction

The study of strongly intramolecularly H-bonded molecules has given rise to numerous theoretical and experimental papers, namely on malonaldehyde [1–4] and acetylacetone [5–18]. Indeed they are the simplest molecules exhibiting an intramolecular hydrogen bond with a proton-tunnelling exchange between the oxygen atoms. Fig. 1 illustrates the keto–enol equilibrium of acetylacetone which is totally shifted toward the enol form

in matrix. It also shows the seven isomers of the non-chelated enol form, labelled nCi , $i = 1, \dots, 7$, whereas the chelated form is labelled C.

Theoretical works have studied mainly the proton transfer between the two oxygen atoms [12,13], the compatibility between theory and experiment [19], or the strength of the H-bond [14], but few studies, as noticed recently by Nakata et al. [7], have been done on the UV photoisomerization of the enol isomer [3,7], and none, to our knowledge, on the IR photoisomerization of the non-chelated forms which are induced by UV irradiation.

The aim of this Letter is to show first results concerning both UV and IR photoreactivities of the non-chelated species. IR photoreactivity is

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proving to be very rich and opening new ways for the understanding of reactional paths in the electronic ground state. On the other hand, when as-

sociated with calculations it is, as demonstrated before on intermolecularly H-bonded systems [20,21], a useful tool for vibrational assignments.

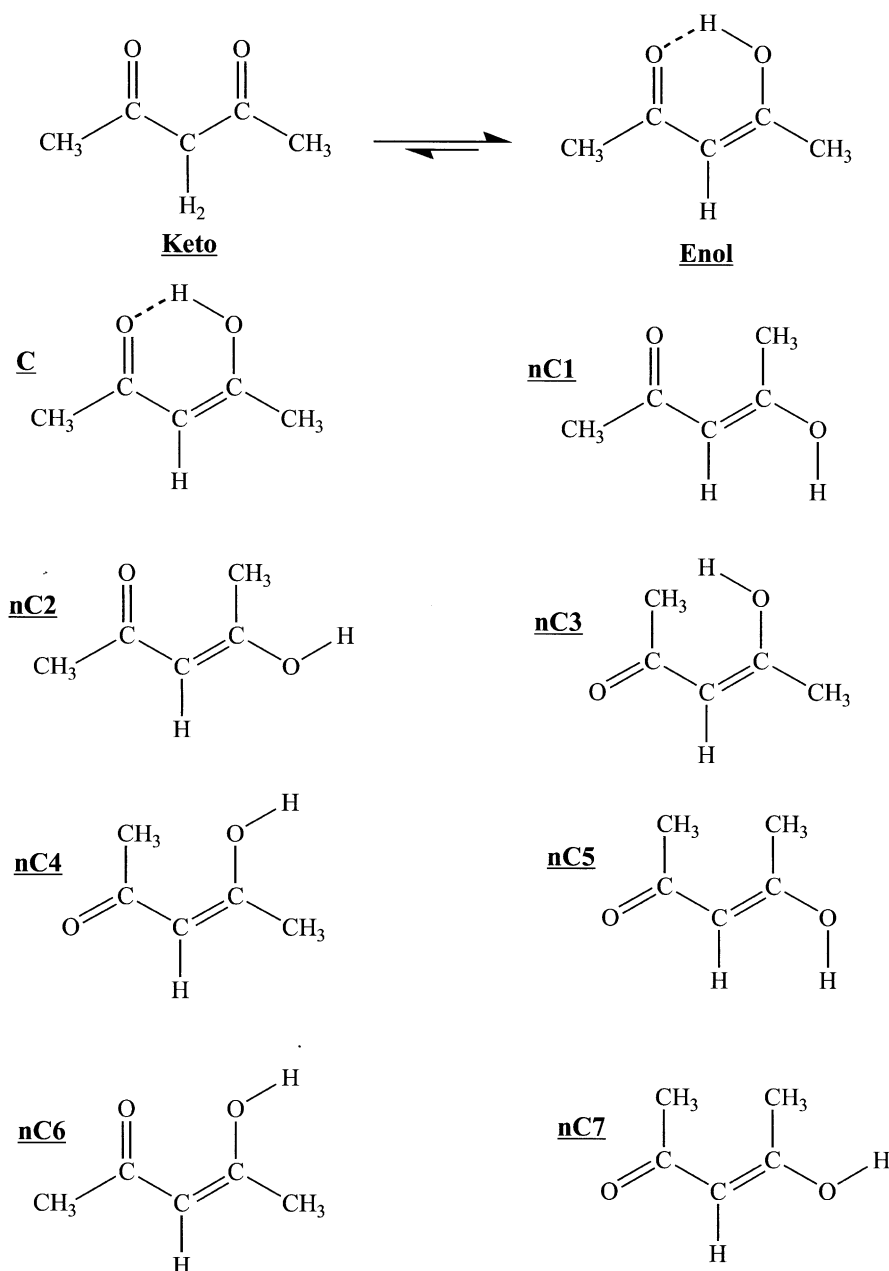


Fig. 1. Keto-enol equilibrium; Scheme of the chelated (C) and of the 7 non-chelated forms (nC) of the enol isomer. The structures are energetically ordered as follows C < nC1 < nC2 < ... < nC7. The energies calculated at the B3LYP/6-311++G(2d,2p) are gathered in Table 1.

The first part of the discussion is devoted to the UV irradiation of the C form and also to that of the nC forms created by this first irradiation. Once the nC forms created, IR irradiations have been performed on their OH stretching modes. Annealings of the sample have been done, after UV and IR irradiations, having important effects on the future reactivity. This will be discussed in a second part and an example of IR irradiation leading to a partial vibrational assignment is given in the last part.

2. Experimental

Acetylacetone (AA) vapor ($C_5H_8O_2 > 99\%$ purity (Aldrich–Chemie) distilled under vacuum) and nitrogen (Air Liquid N60 grade) gas were mixed in ratios $(AA/N_2) = (3/1000)$ (IR) and $(AA/N_2) = (1/5000)$ (UV) in a vacuum line using standard manometric techniques. Different experimental setups have been used both in Paris (laboratory LADIR UMR 7075 of the University Pierre et Marie Curie) and Marseille. The mixture was sprayed onto a CsI window, a highly polished Ni-plated copper or Au-plated copper cube maintained at 17 K by closed-cycle helium cryostats (CTI-Cryophysics or Cryomech PT-405, Marseille; Air Products CSW 202, Paris). The IR spectra were recorded at 10 and 4 K in the transmission-reflection mode using three different interferometers: spectra between 4000 and 20 cm^{-1} were recorded at 10 K with a Bruker 120 FTIR spectrometer equipped with InSb, MCT and

bolometer detectors (Paris). Spectra between 4000 and 500 cm^{-1} were recorded at 10 or 4 K with Nicolet 7000 or Bruker IFS 66/S spectrometers equipped with a MCT detector (Marseille). All the spectra were recorded at a 0.1 cm^{-1} resolution. Two irradiation sources were used: an Oriel high-pressure 200 W mercury lamp (Paris, Marseille) and a BMI (Thalès) pulsed tunable UV–Visible–IR OPO laser (Marseille) (average power, UV: 8 mW; IR: 10 mW). The radiation bandwidth was less than 5 cm^{-1} , pulse duration $\simeq 15\text{ ns}$, repetition rate 10 Hz and tuning range 225–800 nm, 2.7–4 μm . UV spectra were recorded at 17 K in the transmission mode using a SAFAS 190 DES spectrometer.

3. Results and discussion

In our experiments at AA/N₂ molar ratio of 3/1000 the signals observed between 4000 and 20 cm^{-1} are assignable to the monomer. Since the vibrational spectrum of acetylacetone trapped in inert matrices is well identified [3,7,9] we have focused our attention on UV and IR selective irradiations and thermal effects. In support of our vibrational analysis of the new created species, we have also performed ab initio calculations at the B3LYP/6-311++G(2d,2p) level of theory using GAUSSIAN 98 program [22]. This latter theoretical work will be reported in details in a forthcoming publication. Table 1 summarizes the total and the relative energies of C and nC (see Fig. 1), while the calculated frequencies are gathered in Table 2.

Table 1

Ab initio calculated Energies (E in hartree) and energy differences (ΔE in kcal mol^{-1}) between the non-chelated (nC) and the chelated (C) forms of acetylacetone obtained at the B3LYP/6-311++G(2d,2p) level of theory

Isomers	E	ΔE^a	ΔE_{nC}^b
C	−345.9242151	0	–
nC1	−345.9065852	+11.06	0
nC2	−345.9054490	+11.77	+0.71
nC3	−345.9039147	+12.74	+1.67
nC4	−345.9026040	+13.56	+2.50
nC5	−345.9014249	+14.30	+3.24
nC6	−345.8994304	+15.55	+4.49
nC7	−345.8977905	+16.58	+5.52

$$^a \Delta E = E_{nC_i} - E_C$$

$$^b \Delta E_{nC} = E_{nC_i} - E_{nC1}$$

Table 2

Calculated frequencies (in cm^{-1}) of the ν_{OH} , $\nu_{\text{C}=\text{C}}$ and $\nu_{\text{C}=\text{O}}$ vibrational modes, obtained at the B3LYP/6-311++G(2d,2p) level of theory, of the chelated (C) and the non-chelated forms (nC) of the acetylacetone

	ν_{OH}	$\nu_{\text{C}=\text{O}}$	$\nu_{\text{C}=\text{C}}$	$\Delta\nu^a$
C	3212.7	1674.2	1643.3	30.9
nC1	3797.4	1734.1	1635.6	98.5
nC2	3826.4	1738.7	1657.4	81.3
nC3	3808.6	1707.0	1667.0	39.9
nC4	3839.2	1711.9	1704.0	7.9
nC5	3801.6	1698.2	1671.2	27.0
nC6	3819.9	1751.0	1668.5	82.5
nC7	3836.0	1703.4	1694.4	9.0

$$^a \Delta\nu = \nu_{\text{C}=\text{O}} - \nu_{\text{C}=\text{C}}$$

3.1. UV irradiations

The most salient result of a UV irradiation is the opening of the C form leading to those nC. Fig. 2a gives an overview of the $\Pi \rightarrow \Pi^*$ transition bands of the C and nC forms centered at 265 and 230 nm, respectively, the latter being measured after a UV irradiation carried out with the laser tuned at 265 nm. These latter structures are no longer H-bonded and displays ν_{OH} structured bands between 3650 and 3550 cm^{-1} separated in two groups, one between 3628 and 3606 cm^{-1} , the second between 3594 and 3583 cm^{-1} , hereafter referred as high frequency (HF) and low frequency (LF), respectively (Fig. 2b). As for the C form, it is well known that the strong internal H-bond stabilizes this structure by 12 kcal mol^{-1} [14] and induces a red-shift of about 1000 cm^{-1} with respect to a free OH oscillator, as well as a broadening of the OH stretching band over hundreds of wavenumbers [13], leading it unobservable.

We compare in Fig. 2b the ν_{OH} spectra (a) before and after a UV irradiation carried out (b) with the laser tuned at 265 nm and (c) with a mercury lamp. An UV laser irradiation leads to an integrated intensity ratio greatly in favor of the HF bands with respect to those LF. This deserves the following comment: it is noticeable, on the UV spectra, that there is an overlap between the red part of the nC's band and the blue part of the C's band, and, at the end of a UV laser irradiation on C, thus when there remains little C form in the matrix, the LF bands decrease. This suggests that

at the end of a UV laser irradiation on the C species, photoinduced nC forms are also irradiated, those latter forms being certainly the LF forms. Finally carrying out a UV laser irradiation (at 265 nm) we have succeeded in inducing the complete disappearance of C, while the polychromatic beam of the Hg lamp, even if a bandpass filter centered at 265 nm is used, leads to a photochemical equilibrium in which there are continuously conversions between C and nC.

In the case of laser irradiations, we have also performed irradiation at 230 nm and we have noticed that during the first minute of the irradiation, two photochemical processes are induced, the most important leads to C whereas to a much lesser extent $\text{nCi} \rightarrow \text{nCj}$ conversion is observed, nCj being only HF. For longer irradiation times, there remains just the back conversion, never complete, to the C form.

3.2. Thermal effects

Three types of thermal effects have been carried out: after a UV laser irradiation (at 265 nm), after a lamp irradiation, to study a possible thermal back conversion $\text{nC} \rightarrow \text{C}$, and finally after IR laser irradiations in order the system to recover its initial state. The temperature was comprised between 17 and 30 K.

The case of an annealing after a UV lamp irradiation is displayed in Fig. 3, the main effect is the strong decreases of bands at 3637.4, 3628.0, 3626.4, 3624.6, 3623.6, 3590, 3607.1, 3594.0, 3584.1 and 3583.0 cm^{-1} leading to well structured bands. However no back $\text{nC} \rightarrow \text{C}$ conversion is induced. These effects reflect the rebuilding of the matrix around the photoinduced nC forms, allowing to minimize the potential energy. After a UV irradiation, considering the seven nC forms presented in Fig. 1, the geometrical changes are so large that certainly the new matrix potentials are not all stable. The C cages would have been quite distorted by the rotations, leading to a distribution of geometries in the matrix. The relative intensities of the remaining bands depend on duration and annealing temperatures. These post-UV annealings govern afterwards the following IR inter-conversions between the nC forms: depending on

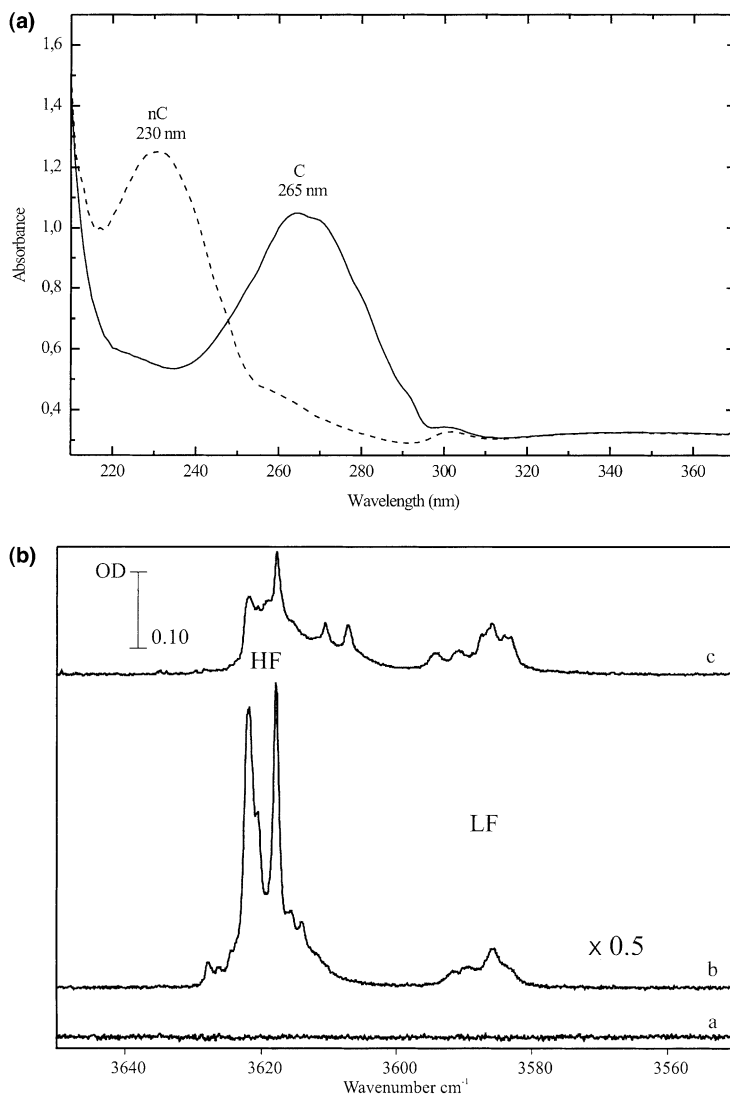


Fig. 2. (a) UV spectra of the C and nC forms recorded at 17 K on samples $[AA/N_2] = 1/5000$. The nC band was obtained after 90 min of laser irradiation at 265 nm. (b) Infrared spectra in the ν_{OH} domain of samples $[AA/N_2] = 3/1000$, (a) at 10 K, before a UV irradiation, (b) at 10 K, after 90 min UV laser irradiation at 265 nm, (c) at 4 K, after 180 min UV lamp irradiation. HF, LF: high frequency, low frequency.

annealing, one observes quite only $HF \rightleftharpoons HF$ photoconversions (Fig. 4), or quite only $HF \rightleftharpoons LF$.

In the case of an annealing after an IR irradiation we observe a partial recovering of the initial state, and not a total recovering as it was already described for other intermolecularly H-bonded systems [20,21], together with further conversions between the nC forms and, no back $nC \rightarrow C$ conversion is induced.

Finally, both post-UV and post-IR irradiation annealings lead to the obtaining of well structured bands and the disappearance of less stable species: a detailed analysis is then necessary to discriminate between site modification or interconversion, the former process having a direct influence on the latter. This, however, puts in evidence the key role of the matrix on the trapped species dynamics.

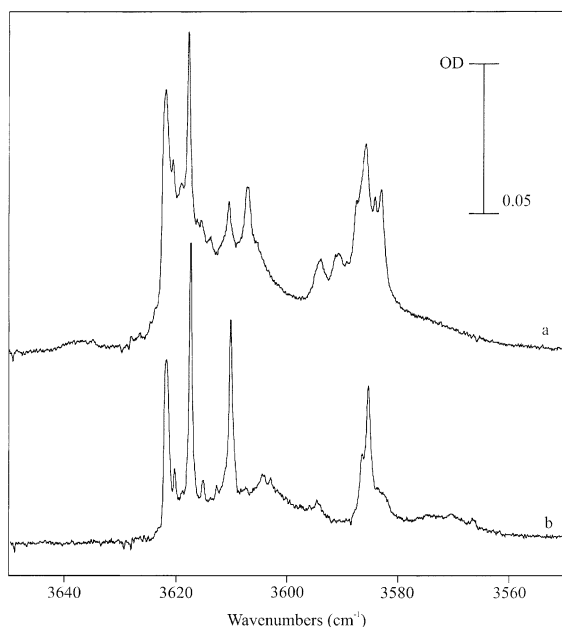


Fig. 3. Annealing to 30 K of a sample $[AA/N_2] = 3/1000$ irradiated by a UV lamp: ν_{OH} domain of spectra recorded at 3.2 K, (a) before, (b) after annealing.

3.3. IR irradiations

The most salient result of these IR selective irradiations is that, carrying out selective irradiations on each band in the ν_{OH} region led to interconversions between the nC forms and not to a back nC \rightarrow C conversion.

We will describe here only one irradiation at 3621.7 cm^{-1} and the complete set of the IR irradiations will be described in a forthcoming publication.

As described above two cases should be studied, before and after a post-UV annealing. In Fig. 4 we show the effect of an irradiation *before an annealing*. This effect is relatively simple to describe, in a rough approximation, as a conversion between the species centered at $3621.7\text{--}3620.0\text{ cm}^{-1}$ and those at $3614.0\text{--}3611.8\text{ cm}^{-1}$. Actually none-less than seven signals centered between 3627.7 and 3618.8 cm^{-1} decrease, only balanced by two increases at 3614.0 and 3611.8 cm^{-1} , and a really weak signal at 3585.7 cm^{-1} . No decisive information in assigning those bands can be retrieved from this OH stretching region except that the two main

decreases are separated by 1.7 cm^{-1} and the two main increases by 2.2 cm^{-1} . The only couples whose OH frequencies are separated by less than 10 cm^{-1} are nC1–nC5, nC2–nC6, nC3–nC5 and nC4–nC7, as deduced from Table 2. Thus we studied the $\nu_{C=O}, \nu_{C=C}$ region and compared the calculated differences $\Delta\nu = \nu_{C=O} - \nu_{C=C}$ with those experimental. Upon this irradiation, three main signals decrease at 1687.6 , 1676.6 and a doublet at $1670.8\text{--}1669.4\text{ cm}^{-1}$ while two intense bands at 1673.1 and 1639.6 cm^{-1} and weakest at 1658.8 , 1648.2 and 1643.2 cm^{-1} , grow (Fig. 4). The two intense increases lead to a $\Delta\nu$ of 33.5 cm^{-1} versus a theoretically predicted 39.9 and 27.0 cm^{-1} for nC3 and nC5, respectively (Table 2). The weak increases lead to relevant differences of 15.6 , 10.6 and 5.0 cm^{-1} , which should be compared with those of nC4, nC5 or nC7. The three main decreases lead to frequency differences of 16.8 , 11.0 and 5.8 cm^{-1} once again comparable with those of nC4, nC5 or nC7. The lack of observed differences of more than 75 cm^{-1} allows us to discard suggested couples nC1–nC5 and nC2–nC6. Finally, to go further in the suggestion of reactional pathways, if we consider that an IR irradiation can only provoke a rotation around single bonds, we can deduce from Fig. 1 that only nC3 \rightleftharpoons nC4 and nC5 \rightleftharpoons nC7 should have occurred. As displayed in Fig. 4, the system totally recovers its initial state upon an irradiation at 3611.8 cm^{-1} .

If we carry out this irradiation *after a post-UV annealing*, the conversion takes place mainly between the HF and the LF forms. In addition to the effects described above, two new strong decreases are identified at 1705.8 and 1630.0 cm^{-1} , while in the ν_{OH} region we observe the increase of the LF bands. The $\Delta\nu$ between the two main decreases is now of 75.8 cm^{-1} which should be compared with those of nC2 or nC6 (Table 2). Moreover, correlated to the increase of the LF bands, we observe new strong increases at $1703.0\text{--}1698.3$ and $1613.6\text{--}1610.9\text{ cm}^{-1}$ giving an average $\Delta\nu$ of 88.4 cm^{-1} , which can be correlated with nC1, nC2 or nC6. The analysis of the only possible interconversions lead to the evidence for a nC1 \rightleftharpoons nC2 reaction in this case.

This example of a resonant ν_{OH} excitation shows the complexity and the richness of the IR induced reactivity of AA, as well as the power of

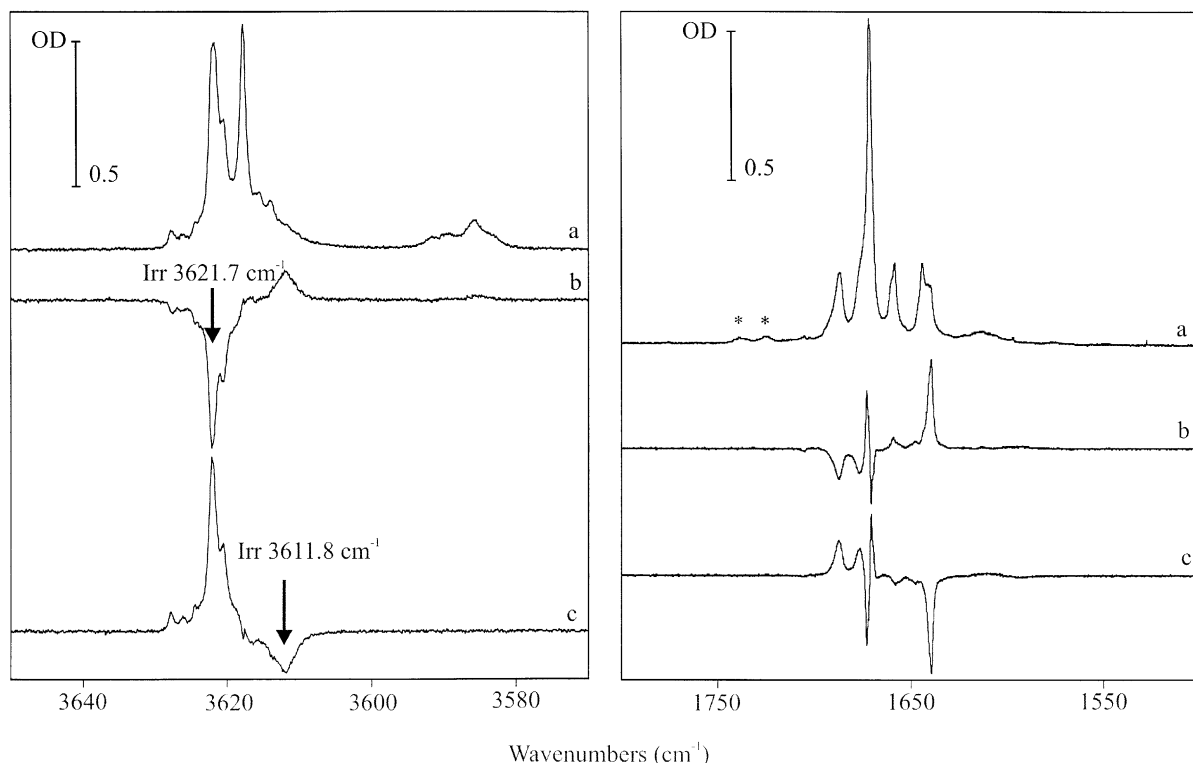


Fig. 4. IR irradiations of a non-annealed sample $[AA/N_2] = 3/1000$: ν_{OH} and $\nu_{C=O, C=C}$ domains of spectra recorded at 10 K, (a) before irradiation; (b) difference after minus before 11 min irradiation at 3621.7 cm^{-1} ; (c) same as (b) for 18 min irradiation at 3611.8 cm^{-1} . * Diketone.

IR irradiations for vibrational assignment of unknown species: when coupled with all the other possible excitations, it opens a large field for studying intramolecular reactional paths.

3.4. Conclusion

UV- following by IR-selective irradiations have been carried out on, annealed or not, samples of acetylacetone monomer trapped in nitrogen matrix. Before a UV irradiation, only the chelated form exists whereas after this irradiation non-chelated forms are observed. In order to suggest a partial assignment for each species present in the matrix, we have compared the experimental frequencies with those calculated at the B3LYP/6-311++G(2d,2p) level of theory. We put under our scrutiny the OH, C=O and C=C stretching regions, in order to discriminate the different set of

vibrational bands of each species. The most relevant results are that we have observed a back $nC \rightarrow C$ conversion only by a laser irradiation at 230 nm, and not by annealing or IR irradiations. We observed interconversions between the nC forms by UV and IR selective irradiations and by annealing.

A deeper theoretical and experimental study should be done to grasp more information on the reactional pathways and to complete the vibrational assignment. This will be presented in a forthcoming publication.

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