

## Photochemical reactivity of matrix-isolated monomeric carboxylic acids

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### Abstract

When used together with conventional spectroscopic methods (e.g. infrared spectroscopy), matrix isolation constitutes a very convenient technique to undertake photochemical studies on single molecules that are not easily accessible to experiment under other sampling conditions, such as carboxylic acid monomers, which show a strong tendency to aggregate. Once a matrix of a given substance has been prepared, in situ irradiation of the target matrix-isolated molecule at a proper wavelength enables the promotion of different types of photochemical processes which, most of times, can also be easily probed spectroscopically. These include conformational interconversions, tautomerization reactions and fragmentation processes (including photodegradation reactions). In this paper, results of both electronic and vibrational photochemical studies carried out on a series of different matrix-isolated carboxylic acid monomers are presented. Besides more conventional techniques, an approach based on irradiation at a frequency matching that of the first overtone of a particular vibrational mode is described. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Photochemical reactivity; Matrix isolation; Infrared spectroscopy; Monomeric carboxylic acids

### 1. Introduction

Matrix isolation spectroscopy has been shown to constitute a very successful approach for studying photochemical reactivity, taking advantage of the very low working temperature — that minimizes the available thermal energy, reducing the probability of occurrence of thermal reactions — as well as from the usual very low concentration of the trapped species and relative rigidity of the matrix that inhibit diffusion and minimize the chance of encounters between the particles [1–6]. As it is relatively easy to start photochemical reactions in a matrix by irra-

diating the sample at specific wavelengths, this technique has unique advantages both for identification and characterization of photochemical reactions (in particular photodegradation and rearrangement reactions) and for the study of photochemically induced conformational isomerization processes.

In the case of carboxylic acids, which have a great tendency to form aggregates under normal experimental conditions, matrix isolation has the additional advantage of enabling the study of the photochemistry of the monomeric species to be undertaken with leisure, since individual molecules can be easily isolated, once the relevant variables (such as matrix gas flow rate and temperature of the substance container) are set properly [4,5].

In this article, some selected photochemical studies on monomeric carboxylic acids, recently undertaken

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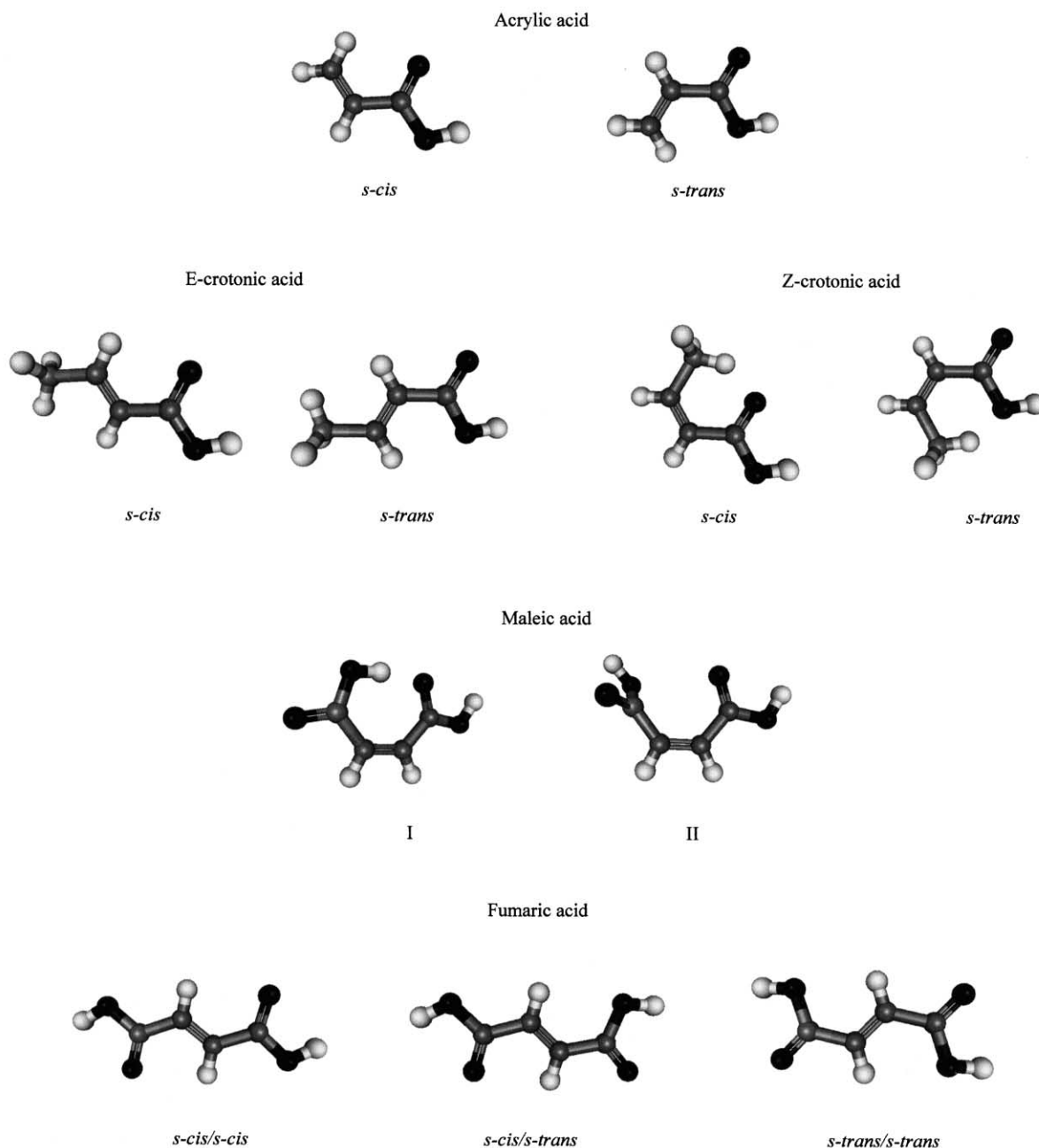


Fig. 1. Most stable conformers of acrylic, (Z)- and (E)-crotonic, maleic and fumaric acids.

in our laboratories, are presented. In Section 3.1, excited state UV-induced photodegradation, tautomerization and conformational isomerization of simple  $\alpha,\beta$ -unsaturated carboxylic acids (acrylic,

crotonic and fumaric acids) are reported. In Section 3.2, ground state infrared-induced reactions are described. Examples of both mid-infrared and near-infrared excitations are provided.

## 2. Experimental

All compounds were obtained commercially spectroscopic grade and purified by standard methods prior to spectra recording. Argon of 99.9999% purity was obtained from Messer Griesheim GmbH or Air Liquide. Depending on the vapor pressure of the substance to be studied, the matrix samples were prepared by different conventional procedures. In the general procedure, the matrices were prepared by co-deposition of argon and the guest compound, the latter being sublimated within the cryostat by using a specially designed mini-furnace connected to a temperature controller (T48 Red Lions Controls) or by continuously flushing with argon a copper tube containing the substance under analysis whose temperature can be varied. The most volatile compounds were pre-mixed with the noble gas before deposition onto the cooled CsI/KBr window of the cryostat (ROK 10-300 Leybold-Heraeus, DMX/DE-202 Displex APD Cryogenics or HS-4 Air Products closed-cycle refrigerators).

The IR spectra ( $4000\text{--}450\text{ cm}^{-1}$ ) were measured with Nicolet SX-60 or Mattson Infinity Series FTIR spectrometers, equipped, respectively, with an MCT detector and a CsI beamsplitter or a DTGS detector and a KBr beamsplitter using spectral resolutions ranging from  $0.25$  to  $1.0\text{ cm}^{-1}$ . Typically 200 interferograms were coadded. Although most of times, the matrix-to-sample ratios could not be determined precisely (when pre-mixing could be done matrix-to-solute ratios higher than 1500:1 were systematically used), we were able to prepare samples in which monomeric species were almost exclusively formed by choosing an appropriate temperature of the substance container and optimizing the matrix gas flow rate.

The irradiation of the samples in the near-infrared (NIR) region was carried out by using a tunable pulsed NIR source, as provided by mixing the  $1.06\text{ }\mu\text{m}$  wave of a Nd:YAG laser (Powerlite 9010, Continuum) with the idler beam of an optical parametric oscillator (OPO Sunlite, Continuum) in a  $\text{LiNbO}_3$  crystal. The pulse duration of the NIR irradiation was ca  $5\text{ ns}$  with a linewidth of  $\sim 0.1\text{ cm}^{-1}$ . The absolute accuracy of the radiation was established to be better than  $1\text{ cm}^{-1}$  by a Burleigh WA-4500 wavemeter used to control the OPO radiation wavelength. In the mid-infrared

region, a CO laser (model ILGN-706) or the filtered radiation produced by the coiled filament (kanthal wire at  $1500^\circ\text{C}$ ) of a conventional IR spectrophotometer was used for irradiation. Ultraviolet irradiation was carried out using the Nd:YAG laser operating at  $266\text{ nm}$  or an UV light filtered source whose main component is a  $500\text{ W}$  Xe arc lamp (Applied Photophysics).

All molecular orbital calculations were made with the GAUSSIAN 92/DFT package of programs [7], installed on a DEC ALPHA 7000 computer, at the Centre of Informatics of the University of Coimbra.

## 3. Results and discussion

### 3.1. Excited state UV-induced processes in monomeric $\alpha,\beta$ -unsaturated carboxylic acids

Simple  $\alpha,\beta$ -unsaturated monocarboxylic acids such as acrylic ( $\text{H}_2\text{C}=\text{CHCOOH}$ ) or crotonic ( $\text{CH}_3\text{CH}=\text{CHCOOH}$ ) acids were shown to exist preferentially in two conformations differing by internal rotation around the C–C bond next to the carbonyl (Fig. 1), the *s-cis* conformation being more stable than the *s-trans* by ca  $2\text{--}3\text{ kJ mol}^{-1}$  [8,9]. In the case of crotonic acid, two different isomers exist differing in the relative position of the methyl and carboxyl groups around the double bond (the *E* and *Z* tautomers, see also Fig. 1). Fumaric acid (*E*- $\text{HOOC-CH}=\text{CHCOOH}$ ) has three conformers of relatively low energy ( $\Delta E < 5\text{ kJ mol}^{-1}$  [10]) differing by the relative orientation of the two carboxylic groups with respect to the C=C bond; the energy of these conformers increases with the number of *s-trans* C=C–C=O arrangements (each *s-trans* axis leads to an increase of energy of ca  $2.3\text{ kJ mol}^{-1}$  [10]). As expected [11], in all these compounds, the most stable conformers exhibit carboxylic groups adopting the *s-cis* (C–O) conformation where the hydroxyl and carbonyl bonds are *syn* periplanar. On the contrary, maleic acid (*Z*- $\text{HOOCCH}=\text{CHCOOH}$ ) exists preferentially in a conformation exhibiting simultaneously *s-cis* and *s-trans* arrangements around the C–C and C–O bonds (see also Fig. 1) due to the stabilizing effect of the intramolecular hydrogen bond established between the two carboxyl groups.

The matrix isolation infrared spectrum of acrylic

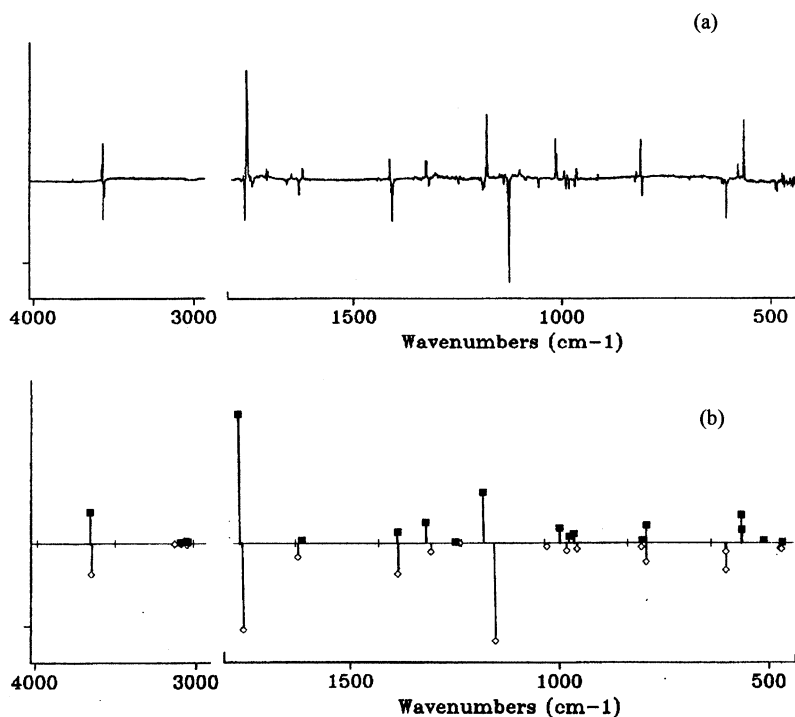


Fig. 2. (a) IR difference spectrum of acrylic acid monomer in an argon matrix (UV-irradiated matrix *minus* non-irradiated matrix). (b) HF/6-31G\* calculated IR spectra of *s-cis* (up) and *s-trans* (down) conformers.

acid clearly reveals that both *s-cis* and *s-trans* conformers are initially present in the sample. Upon in situ irradiation of the matrix at 243 nm, a noticeable redistribution of band intensities is observed. Comparison between the difference spectrum shown in Fig. 2(a) and the HF/6-31G\* *ab initio* calculated spectra of the two conformers shown in Fig. 2(b) unequivocally proves that irradiation converts conformer *s-cis* into conformer *s-trans*. In the case of *E*-crotonic acid, irradiation at the same wavelength leads to occurrence of two different phenomena: (i) a redistribution of intensities of the bands initially present in the spectrum, which are consistent with the presence of the *s-cis* and *s-trans* conformers of *E*-crotonic acid in the freshly prepared matrix and (ii) the appearance of two new sets of bands, with different growing patterns, testifying the appearance of new species. The comparison between the deconvoluted spectra of the observed species with HF/6-31G\* *ab initio* calculated data confirms the presence of the *s-cis* and *s-trans* conformers of *E*-crotonic acid in the initial matrix, the *s-cis*

conformer being converted into the *s-trans* conformer upon irradiation (Fig. 3). In addition, it also enables the precise characterization of the new observed species, which correspond to the *s-cis* and *s-trans* conformers of *Z*-crotonic acid (Fig. 4). Hence, besides internal rotation around the C–C bond next to the carbonyl (C<sub>α</sub>–C), irradiation at 243 nm leads also to internal rotation around the C=C bond, which corresponds to the formal double bond in the ground electronic state. Very interestingly, isomerization of *E*-crotonic acid to *Z*-crotonic acid is faster than internal rotation around the C<sub>α</sub>–C bond. Though either volume restrictions imposed by the matrix or relative masses of the rotating group may also explain this observation, it is more probable that the double bond character of the C=C bond strongly reduces upon electronic excitation and consequently, its associated energy barrier to internal rotation becomes lower in the excited state than that associated with the C<sub>α</sub>–C bond. The same situation might also occur in acrylic acid. However, a definitive answer to this question

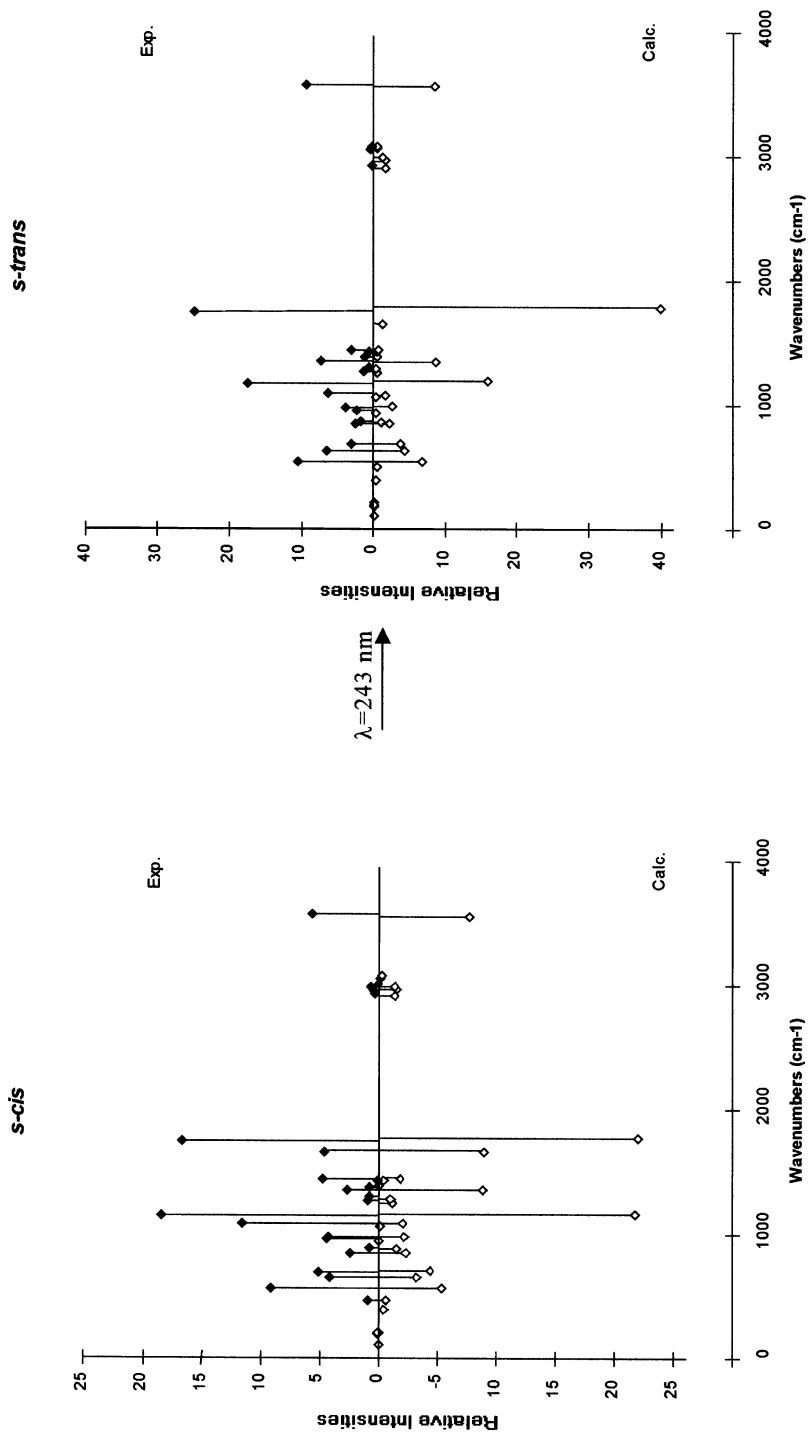
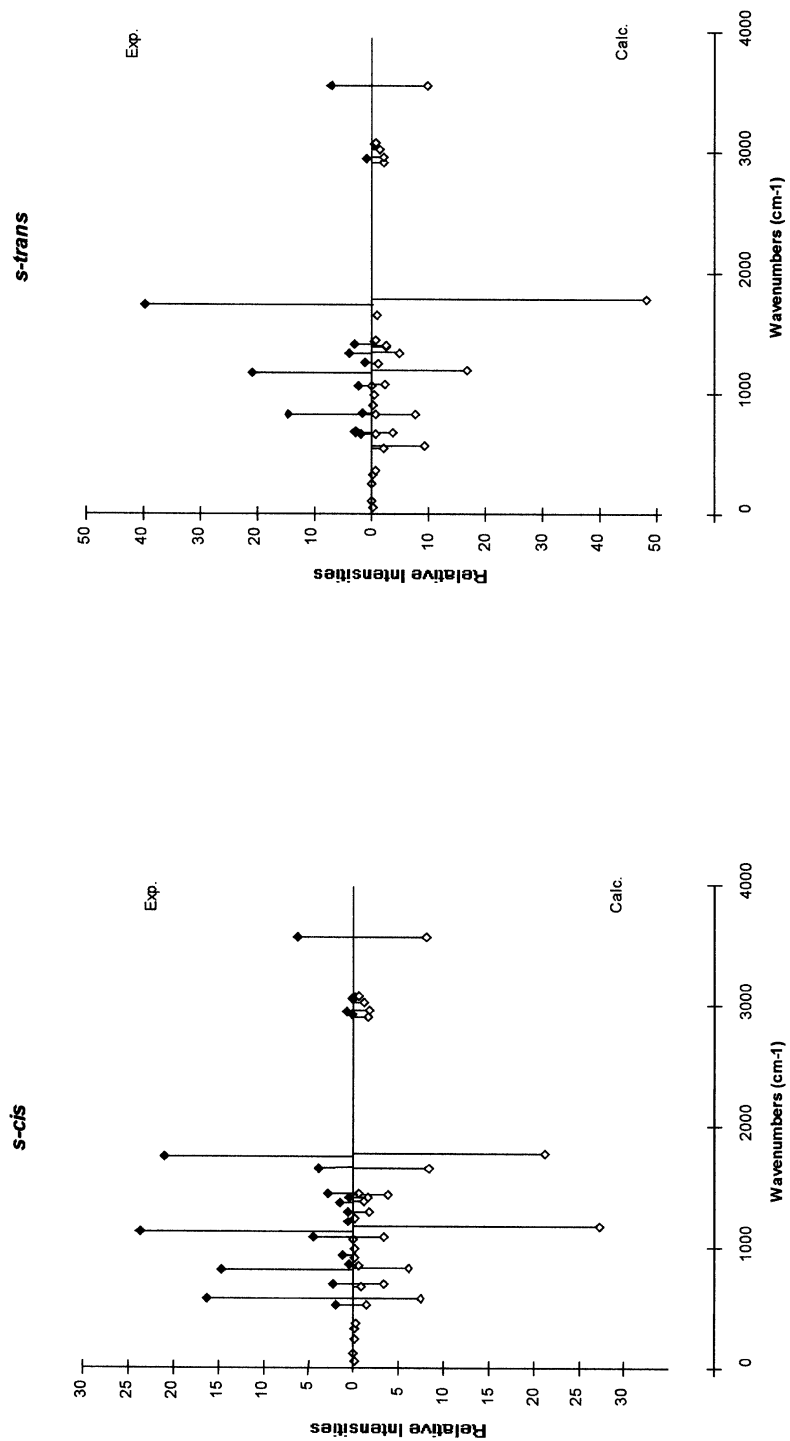


Fig. 3. Deconvoluted experimental and calculated IR spectra of the *s-cis* and *s-trans* conformers of (*E*)-crotonic acid.

Fig. 4. Deconvoluted experimental and calculated IR spectra of the *s-cis* and *s-trans* conformers of (*Z*)-crotonic acid.

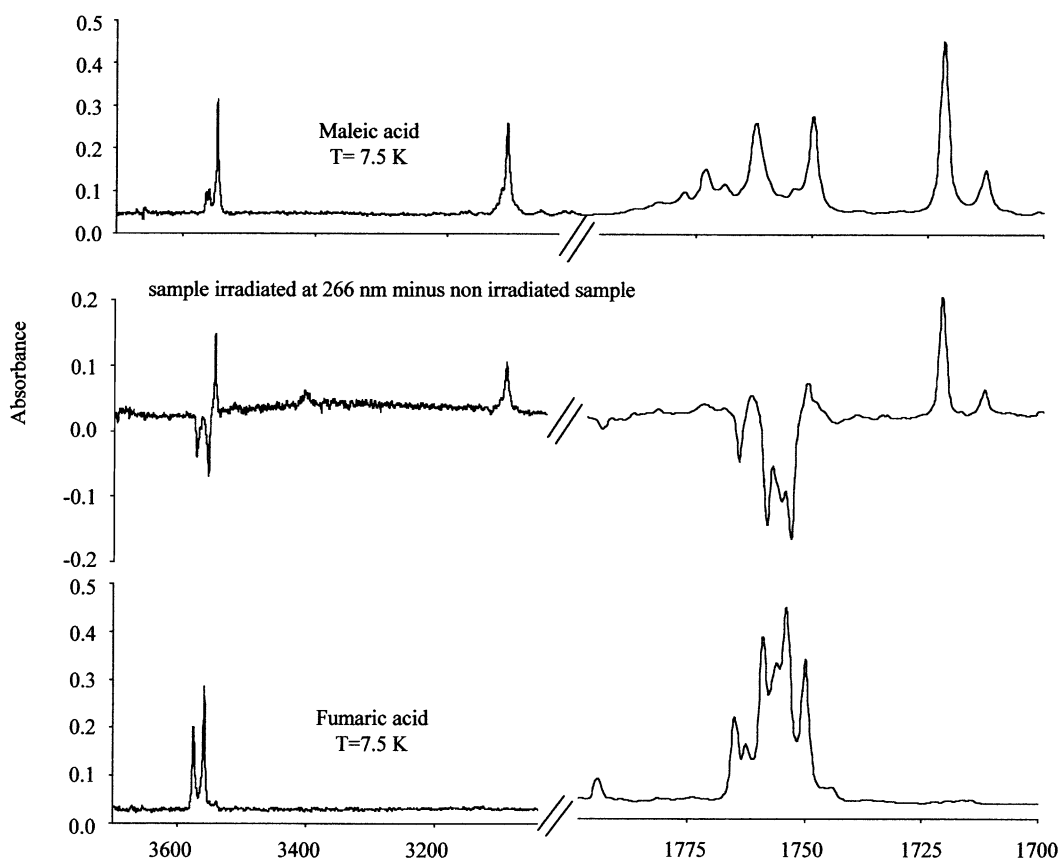


Fig. 5. Matrix isolation IR spectra of maleic (top) and fumaric (bottom) acids and difference spectra obtained by subtracting to the spectrum of a freshly prepared matrix of fumaric acid from the spectrum of the same sample after UV irradiation at 266 nm (middle).

implies the use of selective deuteration of the terminal  $=\text{CH}_2$  group. It is important to note that in hexane solutions the  $\lambda_{\text{max}}$  of the ethylenic  $\pi-\pi^*$  absorption band of acrylic and *E*-crotonic acids are 223 and 219 nm, respectively, with half bandwidths of ca 20–30 nm [8,9] and thus the irradiation was carried out in the long-wave wing of the absorption band. Furthermore, it is well known that the lowest accessible energy excited states in ethylenic compounds correspond, in general, to structures where the relative orientation of the fragments directly connected by the bond, which is formally a double bond in the ground state are nearly perpendicular to each other [12,13].

In the case of fumaric acid, irradiation at 266 nm efficiently promotes isomerization to maleic acid (Fig. 5) while no detectable conformational interconversion between the three conformers present in the matrix

could be observed. These results are also in consonance with a lower excited state energy barrier for internal rotation around the central C–C bond in matrix-isolated  $\alpha,\beta$ -unsaturated carboxylic compounds when compared with the barrier associated with the rotation around the  $\text{C}_\alpha$ –C bond. A similar photochemically induced tautomerization reaction was also previously observed for matrix-isolated fumaryl chloride ( $\lambda_{\text{excitation}} = 340$  nm was used [14]). In this case, maleoyl chloride was produced and as for fumaric acid, no conformational interconversion between the conformers initially present in the matrix could be observed.

In all the compounds studied, it was also possible to promote photodegradation reactions. Characteristic bands of decomposition products, such as CO, CO<sub>2</sub>, HCOOH and H<sub>2</sub>O, are easily observed in the spectra.

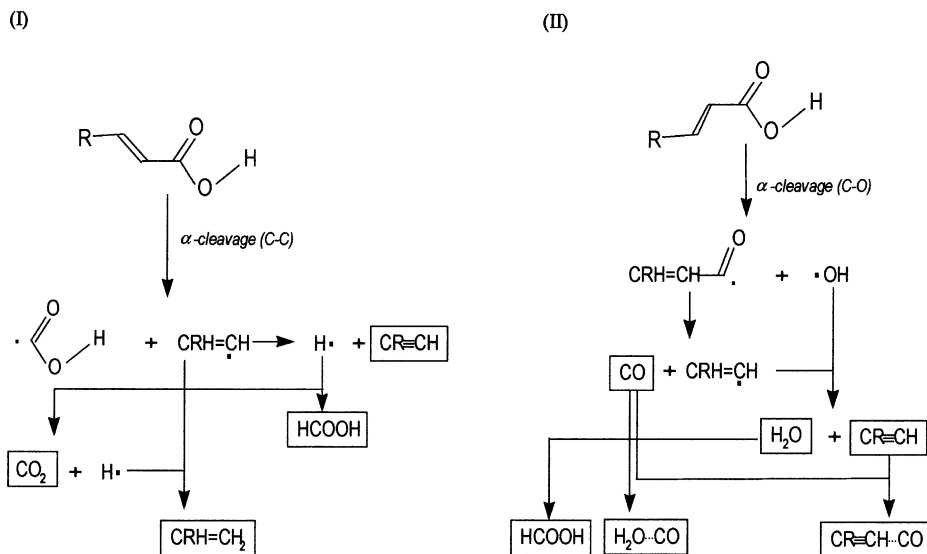


Fig. 6. Main pathways for UV-induced photodegradation processes of an  $\alpha,\beta$ -unsaturated carboxylic acid in an argon matrix.

As the reactant molecules correspond to isolated species, the photochemical transformations pertain to reactions confined to the matrix cage. This fact and stoichiometric considerations [5,6] imply that two different main pathways for photodecomposition of the studied compounds are accessible under these experimental conditions, their relative importance being dependent on the conformation assumed by the reactant molecule (a detailed discussion of the relevance of the conformation of the reactant molecule in determining the preferred pathway for photodegradation of matrix-isolated  $\alpha,\beta$ -unsaturated carboxylic acids can be found in Ref. [6]). For a *s-cis* conformation around the  $C_{\alpha}$ -C bond, the preferred reaction pathway (I in Fig. 6) implies the cleavage of this bond and leads mainly to production of  $\text{CO}_2$  and formic acid (which may further decompose to, for example,  $\text{CO}_2 + \text{H}_2$  upon irradiation [6,15]). In consonance with the higher abundance of the *s-cis* conformer in the matrices of acrylic acid and *E*-crotonic acid [8,9], these were found to be the main reaction products in both the cases. For an *s-trans* conformation around the  $C_{\alpha}$ -C bond, pathway II in Fig. 6 (starting with cleavage of the C-O bond) is prevalent, which is the main source of both CO and  $\text{H}_2\text{O}$  (minor observed products). It should also be pointed out that pathway II may also contribute to

the formation of formic acid though the main route to this species is certainly pathway I. In addition, there is also evidence that secondary dark reactions leading to formation of complexes involving CO also take place under these experimental conditions as revealed by the observed frequencies of the CO stretching mode [16–18].

In the case of fumaric acid, the main process of photodegradation (under 266 nm irradiation) was also found to be the decarboxylation reaction. In this case, two molecules of  $\text{CO}_2$  can be produced in the overall process, which may have acrylic acid as an intermediate.

### 3.2. Ground state IR-induced processes

The use of infrared excitation to promote conformational changes in a matrix-isolated molecule was tried for the first time 37 years ago by Hall and Pimentel [19].<sup>1</sup> The target molecule was nitrous acid ( $\text{HONO}$ ) and the rotamerization reaction was initiated

<sup>1</sup> This was in fact the first study ever reported that was designed strictly to look in detail to this kind of photochemical process, though Baldeschwieler and Pimentel had already discussed this phenomena three years earlier (J.D. Baldeschwieler, G.C. Pimentel, *J. Chem. Phys.*, 33 (1960) 1008) following a previous report by Pimentel (G.C. Pimentel, *J. Am. Chem. Soc.*, 80 (1958) 62).



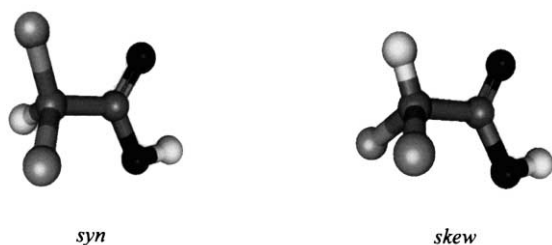


Fig. 7. Most stable conformers of dichloroacetic acid.

by absorption of radiation matching the OH stretching vibration of the studied compound. Later, many papers were published using the same approach (see, for example, Refs. [1–6] and references therein). In particular, it has been found many often that for carboxylic acid monomers selective irradiation of the OH stretching vibrations are of great utility to study conformational isomerization processes [20–24].

One of the most important advantages of infrared excitation, when compared with UV excitation, to promote conformational isomerization is that the infrared-induced reactions are not usually accompanied by sample decomposition. On the other hand, selective vibrational excitation of individual conformers and mode-selective irradiation is most of times easily accessible in the case of infrared excitation by using fine tuning irradiation sources.

Although the elementary mechanism of IR-induced rotamerization is far from being completely understood, it is generally accepted that the most probable mechanism for energy transfer between the excited modes and the torsional coordinates that lead to conformational isomerization requires a resonant interaction involving high-order overtones of the torsions belonging to the adequate symmetry species [21–26]. There is some experimental evidence that indicates that the excitation energy may also be intermolecularly transferred by migrating around the matrix until it finds a target molecule (photosensitization) in a similar way to that occurring for electronic energy migration in crystals [27,28]. Furthermore, different local environments may define the relative ability of the molecules to isomerize. The reactant sites, which act as energy acceptors in intermolecular energy transfer, are those in which the cage favors relaxation via an internal rotation rather than by competing relaxation processes such as molecular rotation and libration (whenever possible) or exchange of energy with the phonon modes of the host. In turn, the reactant species can be formed from non-reactive molecules by non-reactive relaxation. This is particularly relevant in the case of excitation undertaken in the OH stretching region since it is well known that vibrational relaxation of OH stretching vibrations in a matrix often occur via

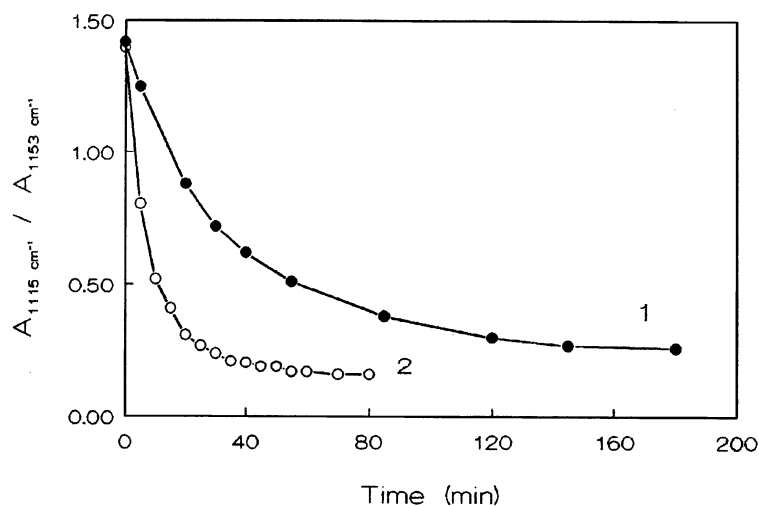


Fig. 8. Dependence of the ratio of the intensity of the IR bands at  $1115\text{ cm}^{-1}$  (*skew*) and  $1153\text{ cm}^{-1}$  (*syn*) at the time of irradiation. (●) Irradiation using the spectrophotometer beam. (○) Irradiation using the monochromator.

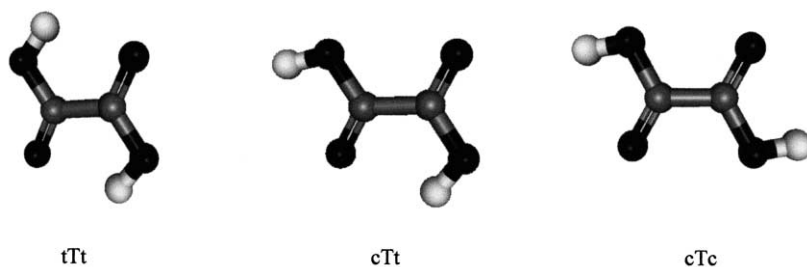


Fig. 9. Most stable conformers of oxalic acid. t and c refer to *s-trans* and *s-cis* conformations of the O=C–O–H axes, respectively, while T and C to the conformation assumed by the O=C–C=O axis (*s-trans* and *s-cis*).

molecular rotation ( $V \rightarrow R \rightarrow$  phonon) [27–29]. So, the production of reactant (“activated”) species is easily accessible and relaxation via internal rotation can be considered as a competitive relaxation pathway whose efficiency depends on various factors including the internal rotation potential energy profile [27].

The relevance of different matrix-trapping sites in determining the reactivity of matrix-isolated molecules towards infrared-induced isomerization is also suggested by the results we obtained for the infrared-induced conformational conversion in dichloroacetic acid [21]. Matrix-isolated dichloroacetic acid exists in

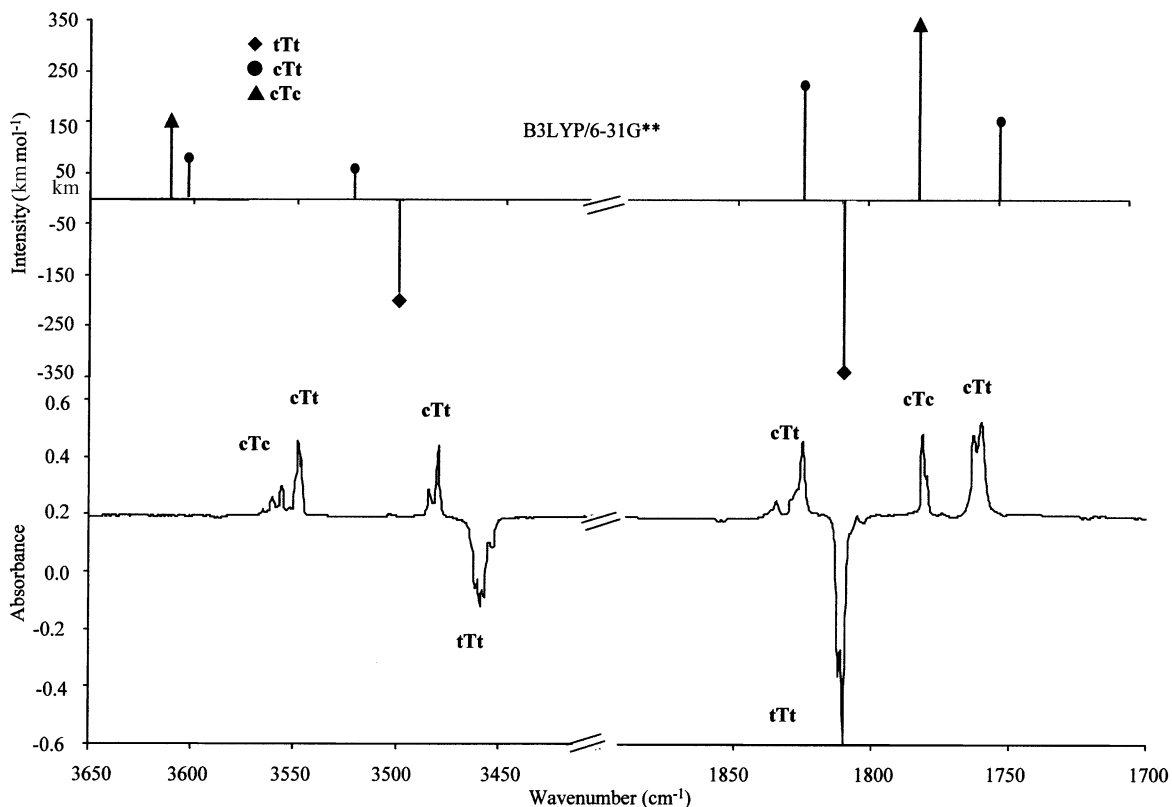


Fig. 10. IR difference spectrum of oxalic acid monomer in an argon matrix ( $6712 \text{ cm}^{-1}$  NIR irradiated matrix *minus* non-irradiated matrix) and B3LYP/6-31G\*\* calculated IR spectra of the three most stable conformers of this molecule (see also Fig. 9).

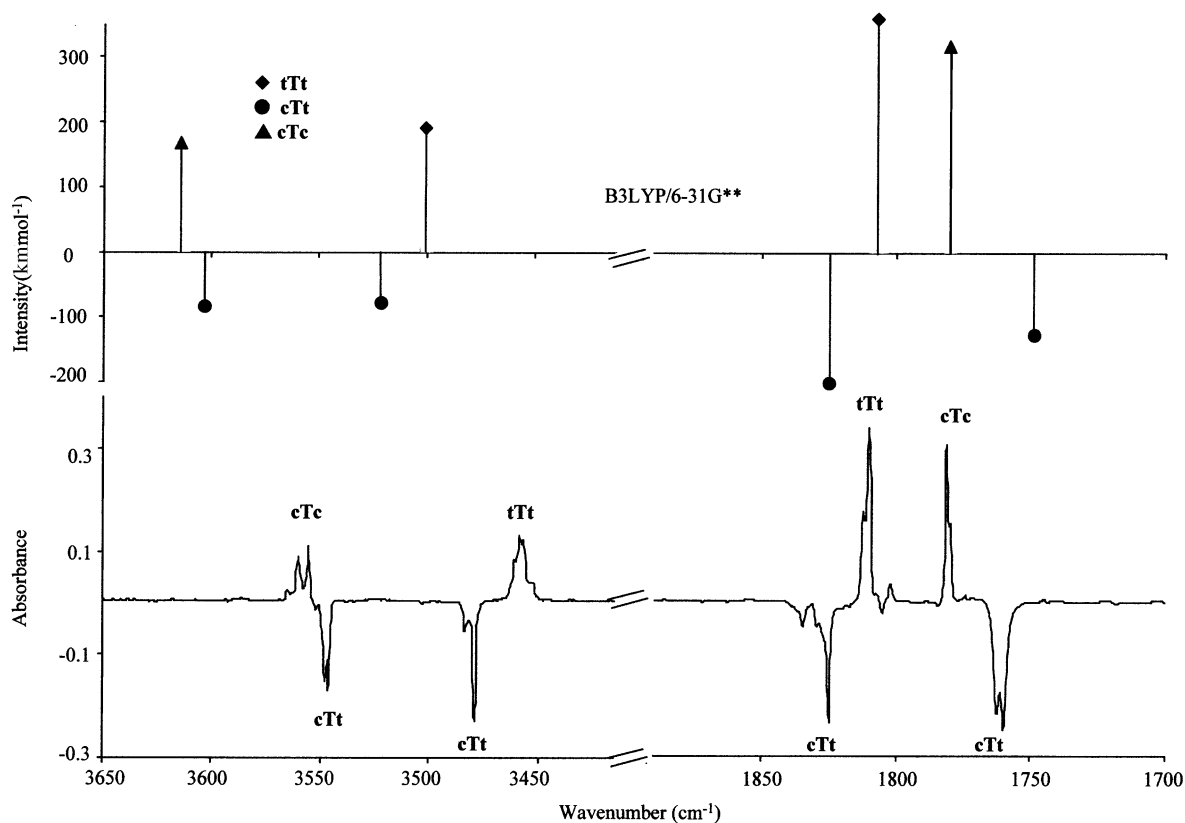


Fig. 11. IR difference spectrum of oxalic acid monomer in an argon matrix ( $6755\text{ cm}^{-1}$  NIR-irradiated matrix *minus* matrix  $6712\text{ cm}^{-1}$  NIR-irradiated matrix) and B3LYP/6-31G\*\* calculated IR spectra of the three most stable conformers of this molecule (see also Fig. 9).

two conformers of nearly equal energy (Fig. 7). Irradiation of the matrix in the OH stretching region causes conversion of the *skew* conformer into the most stable *syn* conformer. Fig. 8 shows the ratio of the most intense bands assigned to these conformers vs time of irradiation. As usually [27], the rate of rotamerization reaction was found to be close to first order with respect to the intensity of the light used to irradiate the sample. On the other hand, it can be observed that the *skew* conformer does not disappear completely upon irradiation. In fact, the intensity ratio plotted in Fig. 8 tends to ca 0.17 (i.e. taking into consideration the relative absorption coefficients of the bands in the two conformers, the *skew:syn* concentration ratio tends to 0.12). This result may be explained considering that the unreactive *skew* conformer differs from the reactive one due to a site effect (indeed, the residual probe band ascribable to

this conformer has a slightly lower frequency than the original band) being insensitive to irradiation. Note that, in principle, the residual *skew* population might also be due to the simultaneous occurrence of the reverse photoreaction process (*syn*  $\rightarrow$  *skew*). In this case, 0.12 would correspond to the ratio of the reverse and direct photoreaction rates (dark reactions were not observed). However, the variation of the observed  $[A_{skew}(t) - A_{skew}(\infty)]/[A_{syn}(t) - A_{syn}(\infty)]$  ratio with the time of irradiation was found to be different from a single exponential thus favoring the explanation based on a site effect [21,27].

Recently, we have used an approach based on selective near-infrared irradiation at a frequency matching that of the first overtone of the  $\nu(\text{OH})$  vibration or combination bands involving this vibration [10,25,26]. For oxalic acid, this methodology was found to be considerably more efficient in promoting

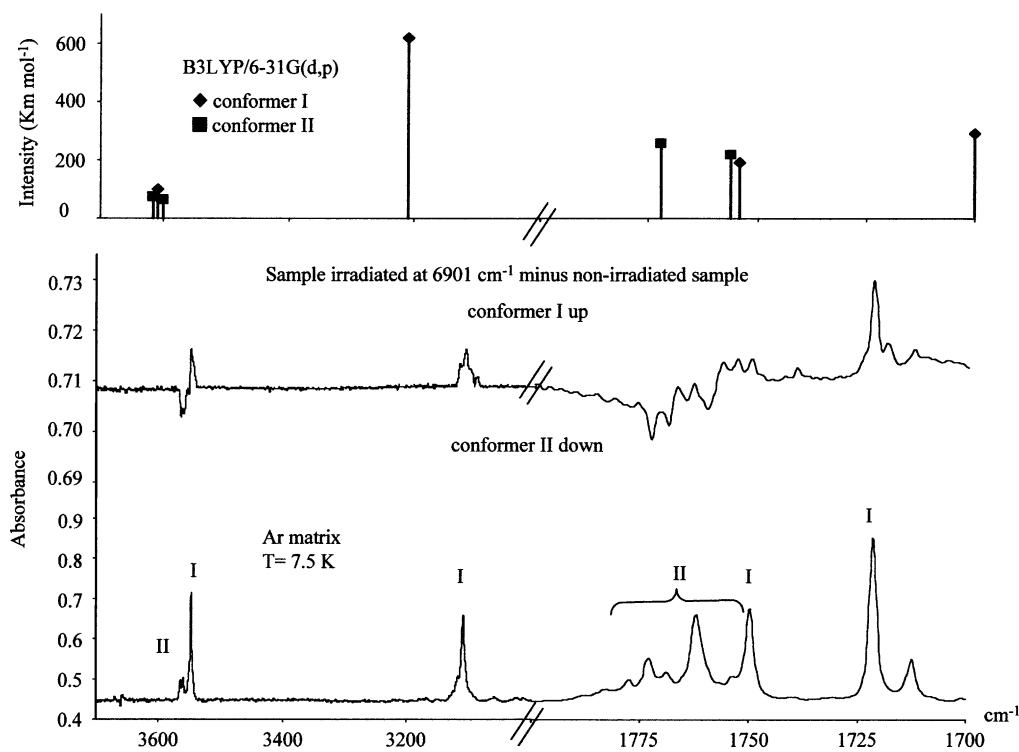


Fig. 12. IR spectrum of maleic acid monomer in an argon matrix, IR difference spectrum ( $6901 \text{ cm}^{-1}$  NIR-irradiated matrix *minus* non-irradiated matrix) and B3LYP/6-31G\*\* calculated IR spectra of the two observed conformers of this molecule (see also Fig. 1).

conformational isomerization than the more conventional approach where irradiation of the fundamental mode is undertaken [22,25], at least in part due to the large amount of energy available to overcome the energy barriers to internal rotations.

Oxalic acid is expected to exist in three conformers observable by matrix-isolation spectroscopy (Fig. 9). Nieminen, Räsänen and Murto have shown that broadband infrared irradiation in the OH stretching fundamental region initiates the cTt  $\rightarrow$  tTt isomerization, though this process was observed to occur with relatively low efficiency [22]. That study enabled only identification of the two lowest energy conformers of oxalic acid. Upon narrow band selective excitation at  $6712 \text{ cm}^{-1}$ , conversion of conformer tTt to conformers cTt and cTc is observed to occur with high efficiency (Fig. 10). Since conformer tTt belongs to the  $C_{2h}$  symmetry point group, the first overtone of its OH stretching modes cannot be pumped by infrared radiation. Nevertheless, the  $\nu\text{OH} + \nu\text{OH}'$  combination

band belongs to the  $B_u$  symmetry species and then can be used as an active vibration to promote photochemical isomerization. On the other hand, irradiation of the sample in the first overtone of the stretching mode of the intramolecularly bonded OH group of the cTt conformer ( $6755 \text{ cm}^{-1}$ ) leads to conversion of this conformer to conformers cTc and tTt (Fig. 11).

Very interestingly, irradiation was shown to be effective in promoting internal rotation about the C–O bonds but no evidence of rotamerization about the C–C bond could be observed despite the rotational barriers associated with the latter process were estimated to be  $<75 \text{ kJ mol}^{-1}$  [30], i.e. lower than that of the excitation energy (ca  $80 \text{ kJ mol}^{-1}$ ). A possible explanation for these findings requires consideration of volume restrictions to the internal rotation imposed by the matrix. Internal rotation about the C–C bond involves the motion of heavy atoms within the noble gas cage, which requires significant reorganization of the matrix. Consequently, the effective energy barriers

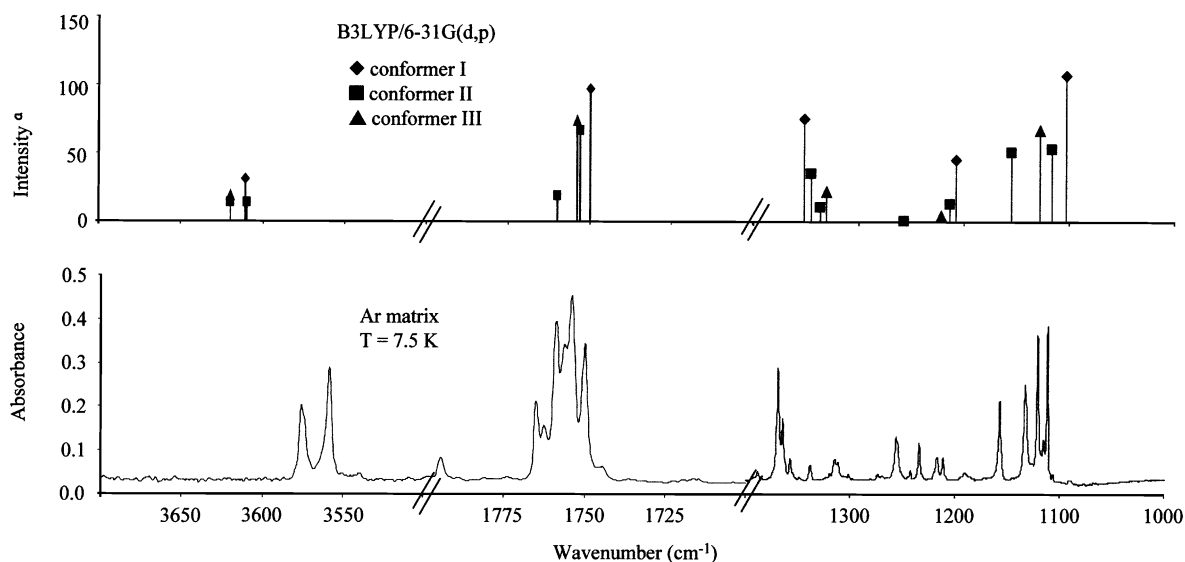


Fig. 13. IR spectra of fumaric acid in argon matrices and B3LYP/6-31G\*\* calculated IR spectra of the most stable conformers of this molecule. Conformers here indicated as I, II and III correspond to the *s-cis/s-cis*, *s-cis/s-trans* and *s-trans/s-trans* forms depicted in Fig. 1.  
<sup>a</sup>Calculated intensities of each conformer were normalized to the sum of the corresponding observed intensities.

for C–C internal rotation in the matrix-isolated molecules may be considerably higher than that for the molecule in vacuum, thus preventing the reaction to occur. An alternative explanation implies that the mechanism of resonant coupling between the OH stretching coordinate and the C–C torsion manifold is not efficient enough to compete with non-reactive relaxation processes and internal rotation around the C–O bonds.

We have also used irradiation in the near infrared region ( $2\nu(\text{OH})$ ) to look at possible conformational interconversion in maleic and fumaric acids. In the case of maleic acid, two conformers contribute to the vibrational spectra of the matrix-isolated molecule. As shown in Fig. 12, selective excitation of the  $2\nu(\text{OH})$  mode of conformer II ( $6901\text{ cm}^{-1}$ ), leads to conversion of this conformer to the most stable conformer I. On the other hand, it was not possible to initiate the reverse reaction by irradiation at the frequency corresponding to the vibrations of conformer I. This conformer has a strong intramolecular hydrogen bond ( $\nu(\text{OH})$ ) in the donor hydroxyl group is red shifted by ca  $450\text{ cm}^{-1}$  relatively to the same mode in a free OH group; see

Fig. 12) and this may be in the origin of the different efficiency of the relaxation through internal rotation in the two conformers upon excitation. For matrix-isolated fumaric acid, excitation in the  $2\nu(\text{OH})$  region does not lead to any observable conformational interconversion process, despite the fact that three conformers could be identified in the freshly prepared matrix [10] (Fig. 13). Since the three lowest energy conformers of fumaric acid differ in the relative orientation of their carboxyl groups, their interconversion would imply the movement of relatively large molecular fragments through internal rotation about the  $\text{C}_{\alpha}\text{--C}$  bonds. So, with all probability the energy barriers associated with these processes are high enough ( $>80\text{ kJ mol}^{-1}$ ) to make them inaccessible under the experimental conditions used. Indeed, these results could be anticipated taking into consideration the above-mentioned results obtained for oxalic acid. A definitive answer to this problem will, however, require a detailed study of infrared-induced isomerization in simpler  $\alpha,\beta$ -unsaturated carboxylic acids, in particular isotopically labelled acrylic acid.

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