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Araştırma Makalesi/Research Article

Photo-Isomerization and Decarboxilation of 2-Amino-5-Chlorobenzoic Acid in Argon Matrix

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Abstract- **In this work, 2-amino-5-chlorobenzoic acid (AClBA) was studied for the first time using matrix isolation spectroscopy in solid argon matrix at 15 K. The molecule has four different conformers, differing by internal rotation about the C–C and C–O bonds. The lowest energy form (O=C-C-C dihedral angle of 0°) was experimentally observed in the IR spectra of the as-deposited AClBA matrices. UV irradiation at λ > 234 nm of the matrix-isolated compound was found to lead to conversion of this conformer into the other conformers and also to decarboxylation of the compound, with production of CO_2. The data of the experimental infrared spectrum results on matrix isolated AClBA were compared with theoretical calculated results.**

Keywords- **Matrix isolation IR spectroscopy, 2-Amino-5-Chlorobenzoic Acid, Photoisomerization, Decarboxcylation.**

I. INTRODUCTION

Benzoic acid is a colorless and one of the simplest aromatic compound containing one monocyclic ring with carboxylic acid group. It is mostly used for food preservative and treatment of certain diseases, for instance, fungus, acne, and tinea [1]. Low temperature matrix isolation infrared spectra of benzoic acid monomers and dimers in argon were studied by Reva and his co-workers. They found that molecule had two conformers with syn and anti form and also, they investigated hydrogen bond interactions by annealing the molecule [2, 3]. 2-chlorobenzoic acid molecule, a derivative of benzoic acid, was examined by matrix isolation spectroscopy and two conformations were found in two different cis positions [4]. UV-induced stimulation of the matrix isolated α-ketocarboxylic acid molecule resulted in less stable conformation with the hydrogen tunneling [5].

Decarboxylation was observed in many matrix isolation experiments. α-pyron was one of the first low temperature studies investigated by the research groups, using matrix isolation spectroscopy [6-9]. As a result of photochemistry of α-pyron, aldehyde ketene (open ring), dewar isomer and decarboxilation of compound were observed and investigated (Figure 1).

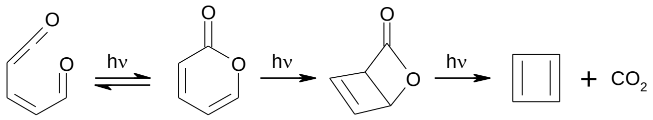

Figure 1. Photochemistry channel of α-pyrone

In our previous study, 2-Chloro-6-fluorobenzoic acid molecule was studied by matrix isolation method. Three different conformers were found depending on the location of the CCOH group. The formation of decarboxylation was achieved with sufficient amount of UV irradiation. 1-chloro-3-fluorobenzene molecule was observed with CO_2 [10] as a photoproducts. Another decarboxila1tion reaction was observed in matrix isolated serine moleküle. When compound was exposed to UV irradiation (λ > 200 nm), CO_2 was observed around 2340 cm^{-1} and also other photogenerated species [11, 12]. As a result of photodecomposition of phenylalanine molecule, the CO_2 product and phenethylamine were observed [13]. Upon laser/MOPO irradiation at 335 and

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345 nm to the matrix isolated N‐Salicylidene‐p‐carboxyaniline, one of the photo products was CO_2. Furthermore, experimental process, decarbonylation reaction occured and CO characteristic band was observed about 2130 cm^{-1} spectral region [14].

In this study, matrix isolation experiments of 2-amino-5-chlorobenzoic acid were done based on the principle of trapping molecules into the cell part of the matrix cage without reaction with inert gas. The best of our knowledge, AClBA was studied for the first time by low temperature spectroscopy in argon matrix at 15 K. No data have been reported about the photochemistry of AClBA. UV irradiation at $\lambda > 234$ nm of the matrix-isolated molecule was resulted the conversion of into the other less stable conformers and also to decarboxylation of the molecule, with production of CO_2 and 2-amino-5-chlorobenzene (AClB), whose vibrational frequencies could be identified in the spectra of the UV-irradiated matrix. The analysis of the experimental data on matrix isolated AClBA was supported by extensive quantum chemical calculations .

II. PHOTOCHEMISTRY OF ISOLATED ACIBA IN ARGON MATRIX

In this study, photochemistry of monomeric AClBA in low temperature matrix was focused and interpreted. Matrix isolation experiments were achieved in Laboratory for Molecular Cryospectroscopy and Biospectroscopy (LMCB) at Coimbra University. The argon matrix was prepared by codeposition of AClBA vapors with nitrogen onto the cold CsI window of the cryostat (15 K). The infrared spectra were taken in the range of 4000−400 cm^{-1}. Compound deposition was finished when the matrix reached a sufficient thickness. The matrix was irradiated with a power of 300 W of 500 W Hg(Xe) arc lamp and recorded after 3, 6, 9, 12, and 15 min of irradiation. When compound was completely deposited in argon at 15 K, only most stable conformer was appeared in the argon matrix spectrum. The other three conformations with high energy were observed after UV irradiation with $\lambda>234$ nm.

The equilibrium geometries of the AClBA molecule and the optimizations of the photo products were run by Gaussian 09 programme [15] using split valans triple zeta basic set density functional theory (DFT) with the 6-311++G(d,p) basis set [16, 17]. The B3LYP density functional theory, which is the three-parameter used for the calculation of DFT, gradient change correlation of Becke (Becke, 1988) and Lee, Yang, Parr [18–20] was used successfully. Potential energy profile allowed us to obtain four different conformers of the AClBA by interconversion between C-C and C-O bounds. Conformer (I) was computed to be more stable than the other forms by 12.3 (C–C–C=C dihedral angle is 177.8^o), 29.1 (C–C–O–H dihedral angle is 10.4^o) and 38.0 kJ mol^{-1} (C–C–O–H dihedral angle is 356^o) with zero point vibrational energy (ZPE), respectively.

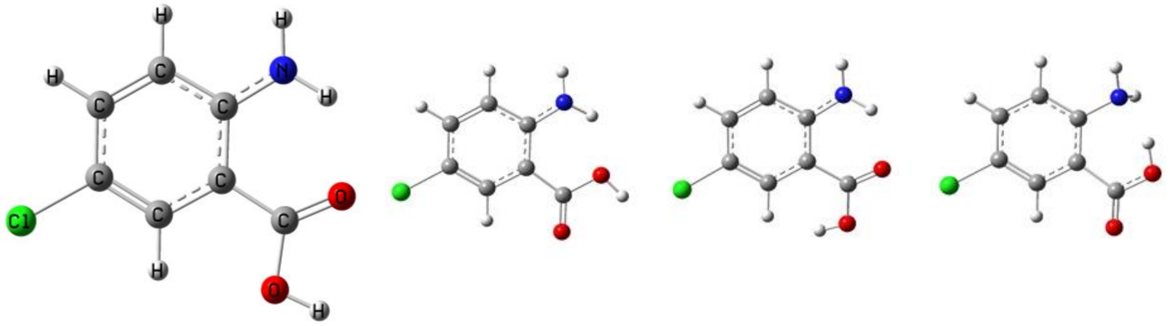


Figure 3. Optimized geometry at DFT(B3LYP)/6-311++G(d,p) of AClBA (most stable form) with symbols and its conformers.

Relative energies and dipole moments of all conformers of the AClBA are given in Table 1. As seen in the table, relative energies and the dipole moment of the conformer IV was found to be higher than other conformations.

Table 1 – Assignments of IR spectra of AClBA (1800-1400 cm^{-1} spectral region) isolated in an argon matrix, and calculated spectra of AClBA conformers using (scaled by 0.978) DFT(B3LYP)/6-311++G(d,p).

	Simetri	**ΔE_{el}**	**$\Delta E_{(ZPV)}$**	**ΔG_0**	**Dipole moment**
AClBA-I	C1	0.00	0.00	0.00	2.24
AClBA-II	C1	12.30	12.27	11.92	4.77
AClBA-III	C1	29.41	29.10	29.15	3.22
AClBA-IV	C1	36.24	38.00	38.45	6.79

The B3LYP/6-311++G(d,p) calculated barrier energies of the conformations are shown in Figure 4. The calculated barrier energy resulting from rotation around the C-C bound was 46.3 kJ mol^{-1}, for reverse processing it was 33.9 kJ mol^{-1} (Figure 3-a). The barrier energies between conformers I → III, II→III and III→IV were calculated 49.7, 51.7 and 26.5 kJ mol^{-1}, respectively. In case of reverse barrier energies were 20.2, 27.7 and 19.7 kJ mol-1, respectively (Figure 3-b, c, d).

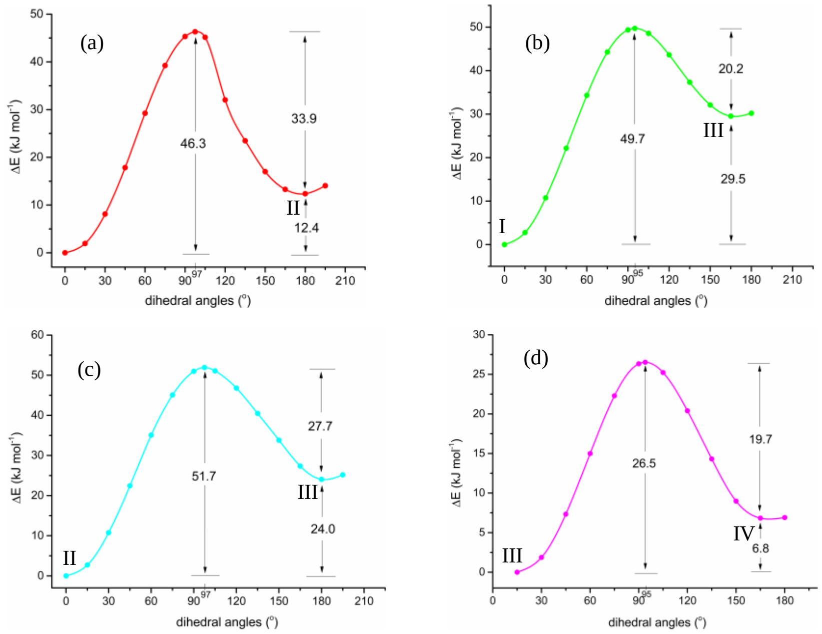


Figure 3. The B3LYP/6-311++G(d,p) calculated potential energy profile for interconversion between C-C (a, d) and C-O (b, c) bonds of AClBA with barrier energies (kJ mol^{-1}).

Matrix-isolated AClBA was exposed to UV-irradiations with different cut-off filters ($\lambda > 375$, 337, 283, 234 nm) or directly to the quartz window. There was not observed any changes in the spectrum while molecule was irradited with $\lambda > 375$, 337, 283 nm. The energy given by UV irradiation was sufficient and since the electrons in the molecule were excited from the ground state to the excited state. However, changes started to occur when the sample was irradiated with $\lambda > 234$ nm. Quantum chemical calculations were used to analyze the spectra for all conformers. After comparing the experimental and calculated spectra, the experimentally observed spectra were determined to belong to the other three conformers II, III and IV (Figure 5 and 6, Table 2). In this case, some of the spectra intensity decreased while the others increased.

Table 2 – Assignments of IR spectra of AClBA (1800-1400 cm^{-1} spectral region) isolated in an argon matrix, and calculated spectra of AClBA conformers using (scaled by 0.978) DFT(B3LYP)/6-311++G(d,p).

Argon matrix 15K	AClBA-I calcaulated		UV-irrad. λ>234 nm	AClBA-II calculated		UV-irrad. λ>234 nm	AClBA-III calculated		UV-irrad. λ>234 nm	AClBA-IV calculated		Assignment
ν	ν	I^{IR}		ν	I^{IR}		ν	I^{IR}		ν	I^{IR}	
1723-1719	1705	410.2	1754-1745	1737	461.8	1740	1734	356.0	1770	1766	374.7	νC=O
1620	1617	117.0	1624	1622	177.3	n.obs.	1618	128.2	n.obs.	1626	27.7	νring(1)
1587	1584	180.1	1605	1603	62.9	1585	1583	160.8	n.obs.	1594	19.4	δNH_2, νring(2)
1557	1549	103.9	n.obs.	1558	19.6	n.obs.	1548	69.7	n.obs.	1566	5.1	νring(3), δNH2
1488	1474	91.6	1498	1479	205	1494	1478	103.0	1490	1474	79.1	δC1-H7, δC6-H9, δC1-H7
1415	1409	15.1	1432-1430	1421	121.7	n.obs.	1411	27.4	1448	1414	417.7	δOH, δC6-H9

Frequencies (ν) in cm^{-1}; calculated infrared intensities in km mol^{-1}; ν, stretching, δ, in-plane bending, n.obs., not observed, see Figure 1 for atom numbers of AClBA.

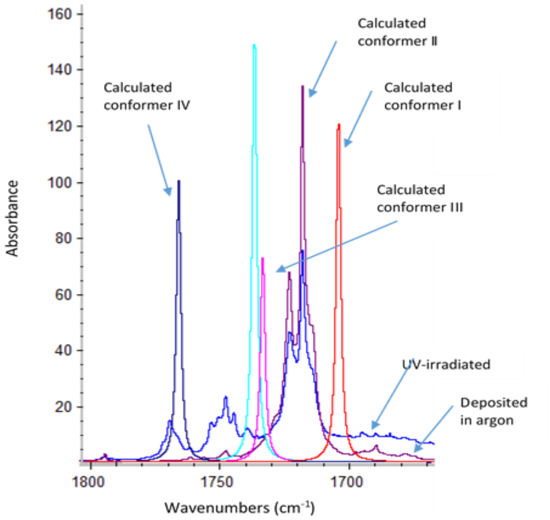


Figure 5. C=O spectral region for deposited compound in argon matrix; UV-irradiated with λ>234 nm and calculated spectra for conformers I, II, III and IV.

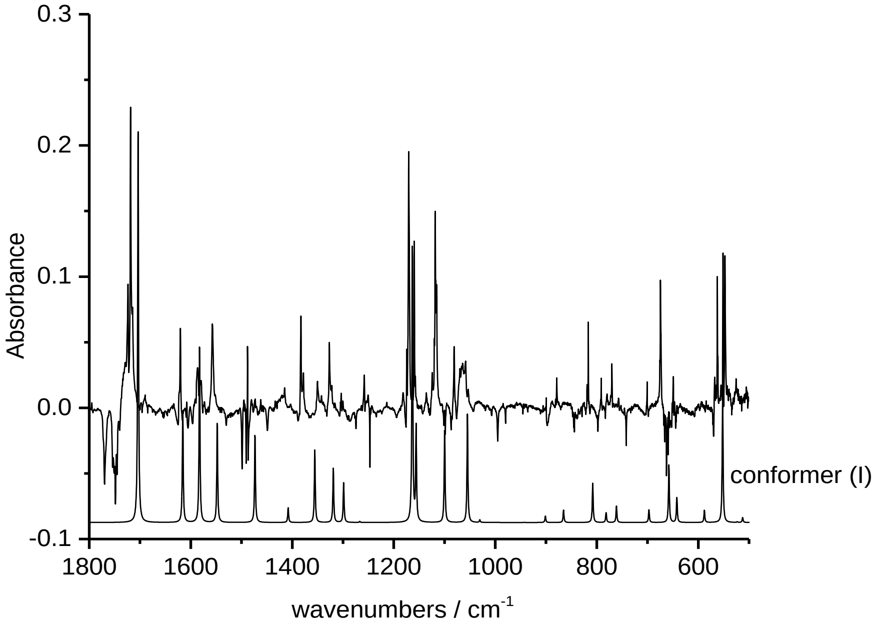
Experimental matrix isolation (deposited and UV-iradiated) spectra and calculated spectra (1800-1400 cm^{-1} spectral region) are given in Table 2. In the table, only the spectral region with a high intensity was taken. It shows that all the conformers are trapped within the argon matrix at 15 K. As can be seen in Figure 5 and Table 2, the C=O region can be compared in detail.

Table 2 – Assignments of IR (UV-irradiated) and calculated spectra of AClB + CO_2 (most intensity spectral region) using (scaled by 0.978) DFT(B3LYP)/6-311++G(d,p).

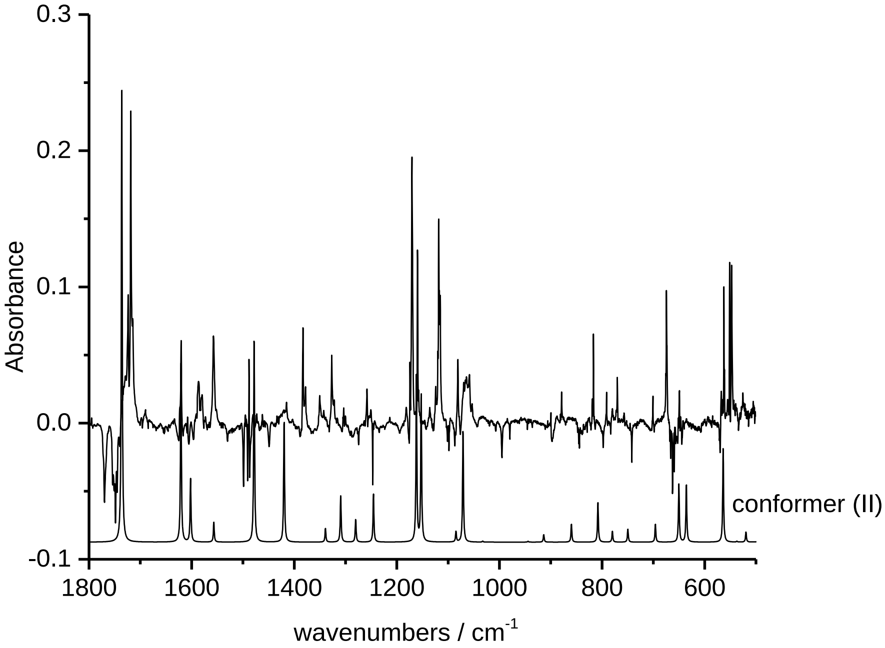
AClB		CO_2		UV-irrad. To quartz	Assignment
calculated					
ν (cm^{-1})	I (km mol^{-1})	ν (cm^{-1})	I (km mol^{-1})	ν(cm^{-1})	
		2365	655	2345	νCO_2
1628	121.8			1624	δNH_2
1491	157.0			1496	νCN, δCH
1273	87.0			1291	δCH

ν, stretching, δ, in-plane bending, see Figure 6 for AClB and CO_2.

The most intense band of CO_2 was observed experimentally at 2345 cm^{-1} and calculated computationally at 2365 cm^{-1} (Table2, Figure 5). Calculated AClB and CO_2 spectrum fits well with the experimentally observed one.



(a)



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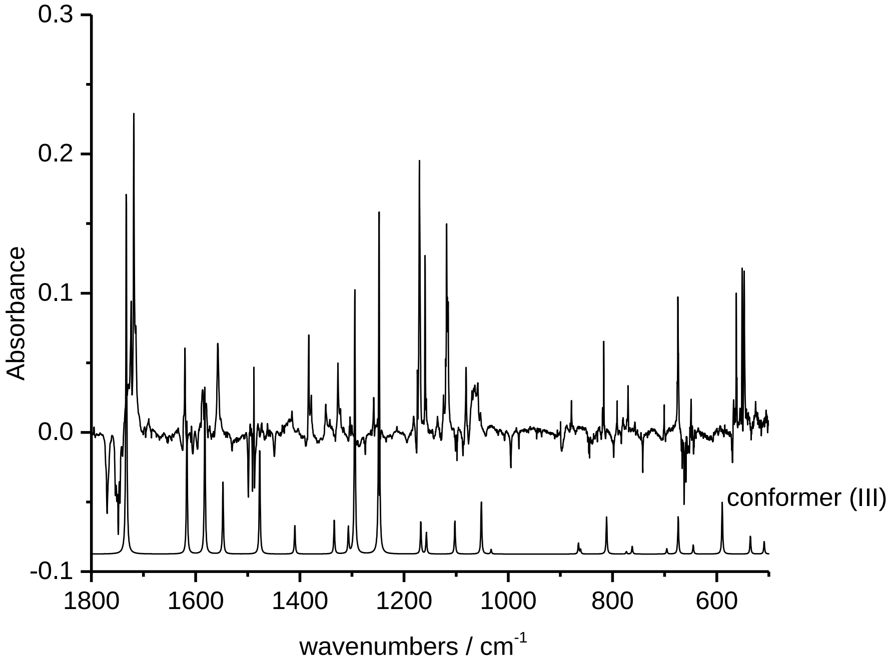

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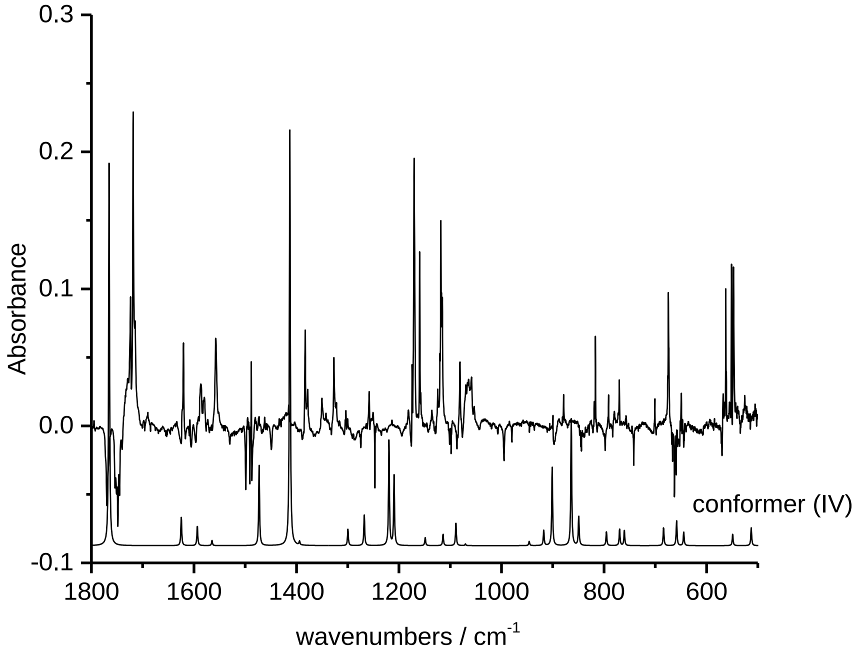

(d)

Figure 6. Difference spectra of experimental matrix isolated AClBA in solid argon minus UV irradiated with λ> 234 nm (top), Calculated spectrum for all conformers at DFT(B3LYP)/6-311++G(d,p) level (conformer I, II, III, IV).

Frequency analysis of the conformers were performed using the data obtained from the result of out file of the Gaussian Program. The results of the analysis are given in Table 2. Upon UV irradiation matrix-isolated compound has been shown directly to quartz, the started to decompose, with evolution of CO_2 and formation of 2-amino-5-chlorobenzene (Figure 7, Table 2) .

In our previous work, matrix isolated coumarin in argon was exposed to UV-irradiation (λ> 200 nm). Decarboxylation of the molecule was observed and products of benzocyclobutadiene and CO_2 [21]. However, in 3-acetamido-coumarin only the open-ring ketene and the decarbonylation reactions were shown in the matrix spectra, while Dewar isomer photoproduction was not occur [22]. Similar results were observed for 2-pyrone-3-carboxylate [23]. UV-irradiation (λ> 234 nm) of the matrix isolated 3-furaldehyde was analysed and resulted in conformational change. When compound was irradiated at higher energy directly to the quartz window, decarbonylation of the compound was obsreved with products of two C_3H_4 isomers (cyclopropene and propadiene), furan, and cyclopropene-3-carbaldehyde [24].

Calculated infrared spectrum by the B3LYP/6- 311++G(d,p) for AClB fit very well with the experimental UV irradiated matrix isolated compound, both concerning intensities and relative position of bands (Figure 6). Before UV irradiation experiments between 7000-2000 cm^{-1}, compound was irradiated with near infrared (NIR) light and overtone (2νO-H) band appeared on the NIR spectra about 6100 cm^{-1} spectral region. The aim was to obtain other conformations of AClBA by exciting the OH band. However, no changes in the spectrum was observed.

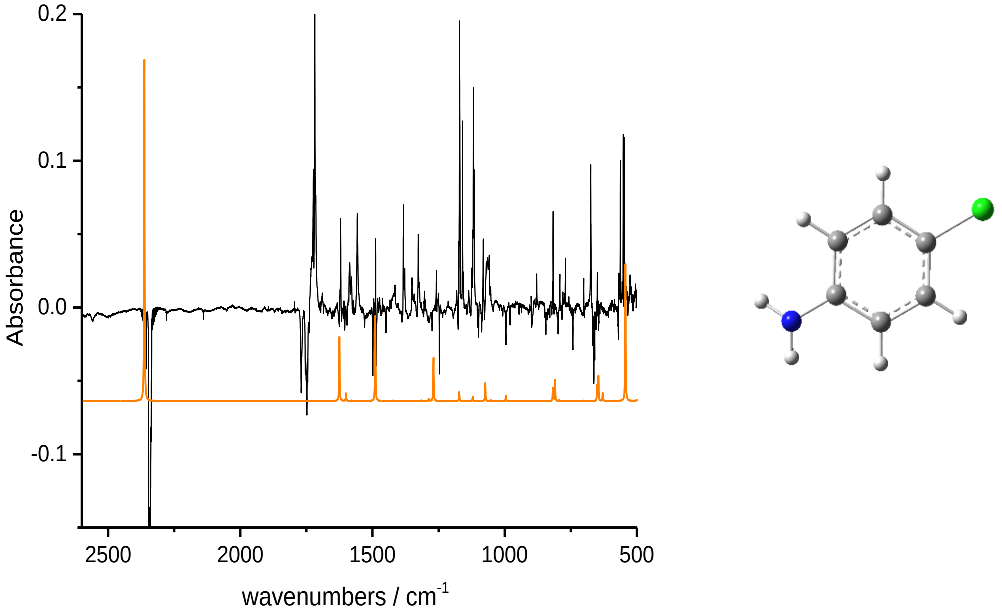

Figure 7. Left: Difference spectrum of deposited minus UV irradiatied AClBA (top) and decarboxylation of the compound, with production of CO_2 and 2-amino-5-chlorobenzene (AClB; below). Right: Scheme of AClB + CO_2

The Spectra with different intensities at different regions were observed after 3 min. in the matrix. Every step of UV irradiation time was increased by 3 minutes. Density functional theory calculations were carried out to evaluate the experimental and calculated data of photoproducts. New peaks appeared with decarboxilation in the spectrum when matrix isolated AClBA was iradiated with UV light just for 3 minutes. The difference spectrum (matrix isolated spectra minus UV-irradiated spectra) of products (Figure 7) were compared with the calculated spectra of AClB. In the calculated results, it was proved that strong CO_2 absorption bands between 2348-2336 cm^{-1} spectral region were in the same region at UV-induced matrix experiment (Figure 8).

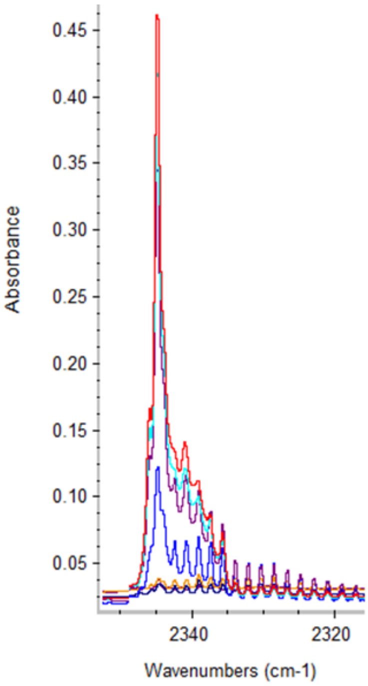

Figure 8. CO_2 absorption bands resulting from UV irradiation (increased by 3 minutes at each step).

III. CONCLUSIONS

In this work, experimental studies of AClBA were performed by matrix isolation infrared spectroscopy in solid argon. The spectra of the four conformations were observed after the molecule was deposited in the solid argon. In order to obtain optimized molecule, *ab-initio* quantum chemical calculations were made on the computer using DFT method and B3LYP hybrid functional with 6-311++G(d,p) basis set. The minimum energies of the four conformers were found from the potential energy calculation results and their infrared spectra were plotted to compare with the experimental results. Four different conformers were observed using in situ UV irradiations (λ>234 nm) in a low temperature (15 K) argon matrix spectra. As a result of the decarboxylation reaction, new photo product, AClB and CO_2 were observed at the same time with conformers. The results of the experiment were well matched to the calculations. The experiment thought to be repeated in the future, using NIR light sources in the nitrogen or xenon matrices to investigate if different photoproducts can be formed.

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