



Formic Acid Ionization and Fragmentation by Multiphoton Absorption

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ABSTRACT

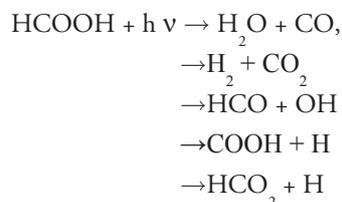
Multiphoton absorption is an intensity dependent nonlinear effect related to the excitation of virtual intermediate states. In the present work, multiphoton ionization and dissociation of the formic acid molecule (HCOOH) by the interaction with photons from 532 Nd: YAG laser at different intensities are discussed, using different carrier gases. The induced fragmentation-ionization patterns show up to 17 fragments and dissociation channels are proposed. Some evidence of small clusters formation and conformational memory from the ratio of the detected products, CO^+ and CO_2^+ , on the light of the available results, it is possible to conclude that they arise from trans and cis formic acid. Our results are compared with those obtained in other laboratories under different experimental conditions, some of them show only partial agreement and differences are discussed. Following the Keldysh description it is possible, from our experimental parameters, characterize our results, in the multiphoton absorption regime.

1. Introduction

Multiphoton absorption processes are an important method to investigate fundamental characteristics of different chemical aspects. In particular, small molecules as the formic acid offers an opportunity to show some properties of such systems. Molecules excited by photoabsorption undergo several photochemical processes. Several experimental and theoretical studies have been reported regarding to formic acid. Among them, molecular dissociation has attracted much experimental and theoretical interest since it is the initiation of many chemical reactions in the atmosphere. Formic acid, FA, HCOOH, is a molecule of concern to both astrophysics and to exobiology. Closely related to possible building blocks of biomolecules, [1] it has been observed by radioastronomy in several sites in the interstellar medium, e.g. in the cold dark cloud L134N, as well as [tentative detection] in W51, a region of the interstellar cloud Sgr B2 [2, 3]. As the simplest carboxylic acid, formic acid has been observed in the upper troposphere of the earth, interstellar medium, and combustion processes [4-6]. The relative abundance of formic acid is at least 50 times greater in protostellarices than in gas phase astronomical sources, including comets, which suggests that the gas phase photostability of formic acid with respect to UV and VUV radiation is much less than for HCOOH embedded in a

solid ice. The photophysical properties of HCOOH in this region are thus of direct interest for understanding such phenomenon, as well as for undertaking radio astronomy searches, for cometary science, and for exa-biology studies. Besides conformational change an important concept in various fields of chemistry and beyond can be addressed in formic acid studies. Formic acid has been widely theoretically studied, through computational methods, the dissociation energies, different dissociation pathways and the possible configurations of formic acid clusters, for both cis and trans formic acid have been characterized [7-14]. Most of the experimental studies had been performed by laser photolysis to produce vibrational excited products. However, there are several experiments on ionization and dissociation using different projectiles, as electrons, protons or photons [15-21].

The five dissociation channels that can possibly occur in the photolysis of formic acid are:



Most of the ionic species have been observed in experiments of formic acid destruction by soft X rays [21, 22] inner shell excitation [23] ultraviolet region [10] or the interaction with protons or electrons [19, 28]. In this work, we analyze the mass spectra of the ions obtained as a result of the interaction between formic acid and laser radiation with different intensities of 532 nm radiation, contrasting them with some of the available theoretical and computational results.

2. Experimental

The photofragment spectra from formic acid multiphoton absorption were obtained by a high-resolution time of flight mass spectrometer, a commercial spectrometer [Jordan] modified in the laboratory [26], coupled to a vacuum chamber 60 cm diameter, housing the interaction zone to produce the fragment ions. 2ml of formic acid (Sigma Aldrich, 96% purity) was introduced to a stainless-steel reservoir, where the sample is evaporated. The reservoir is connected to the tube evacuated of the order of 10^{-3} torr. This tube is the bridge between the reservoir and the entrance to the spectrometer chamber and also connects to a valve that allows the entry of the carrier gas as required by the stage of the experiment. The formic acid seeded with He or Ar was introduced through a pulse valve. The pulse valve has an extension with a conical tip termination inside the chamber that allows the adiabatic gas expansion closer to a skimmer for the generation of the supersonic molecular beam. A heated molecular beam of formic acid /He or Ar was produced by adiabatic expansion in a high-vacuum chamber at 2×10^{-7} torr. The pulsed valve was synchronously coupled with the laser pulses with an opening time of 180 μ s in order to ensure that the formic molecules and laser light coincide at the center of the interaction zone. The operating pressure was: 2×10^{-6} torr. The 532 nm laser radiation was produced from the second harmonic of a Nd: YAG laser (Spectra Physics), operating at 30 Hz repetition rate. The laser pulse width is 5.5 ns and the energies per pulse from 1 to 30 mJ. The laser radiation (with a Gaussian profile and vertically polarized) was focused into the interaction region using a 15 cm focal length lens. The diameter at the focal point was 80.0 μ m. Under these experimental conditions, radiation intensities between 10^9 and 10^{10} W \cdot cm $^{-2}$ were achieved. The molecular beam interacted orthogonally with the laser radiation at a point located between two parallel plates continuously polarized at 5.0 keV and 3.5 keV, corresponding to the extraction and the acceleration potentials, respectively.

The distance between the plates was 0.6 cm. Holes of 10 mm diameter at the center of each plate covered with a fine metal mesh were used to extract the positively charged

ions from the interaction region. The ions were driven along the field-free region of the RTOF analyzer and they reached a dual Chevron microchannel plate detector after they were refocused. The ionic products were extracted from the interaction region at a potential of 1.5 keV which is the potential difference between the two plates that limit the source of ions and accelerated towards the second chamber of the spectrometer, the drift region or free zone of field where the ions are separated according to their m/z values. The ions arrived to the detector, according to the ratio masses/charge (m/z). The resolution achieved was of the order of 1000. The current signal was pre-amplified, voltage-converted, digitized and sampled in time using a picosecond time analyzer from EG&G ORTEC.

3. Results and Discussion

A detail calculation on the dissociative profiles of $S_0, S_1,$ and T_1 surfaces for the photodissociation of HCOOH are reported on [9] and the analysis of the dissociation mechanisms of FA at 248 nm and 193nm They show the different accessible radical channels. The potential energy profiles correlate to the products with the energy of 4.42, 4.03 and 4.87 eV higher, and a discussion was made at laser energies of 248 nm and 193 nm. In our case with a laser wavelength of 532 nm 2.33 eV, multiphoton absorption is required to reach the various the proposed channels and ionize the resulting products. In our case the with a laser wavelength of 532 nm 2.33 eV multiphoton absorption is required to reach the various channels proposed and ionize the diverse products. Accordingly to the atomic model were γ , the adiabatic Keldish parameter [26] which characterizes the regime of the laser- molecule interaction: Multiphoton Ionization [MI], tunneling ionization (TI) or and over the barrier ionization (OTBI) depend on I_p the molecular ionization potential (in eV in absence of a laser field, I is the laser intensity[in W/cm 2]) and λ is the laser wavelength (in μ m) through the expression:

$$\gamma = [I_p / [1.87 \times 10^{-13} I \lambda^2]]^{1/2}$$

Values of γ higher than 1 are indicative of MPI mechanisms dominating the ionization process, whereas values lower than 1 imply the participation of field-ionization mechanisms. In the present study γ higher than 1. Although the processes could be a mixture contain contributions from both MPI/ATI and less contribution from ATI, however this issue demands further consideration. DeWitt [27] have addressed the dependence of dissociation yield with molecular size, however until the present, Keldysh theory is applied. More than 20 different cations were observed corresponding to some dissociation channels already proposed [22]. Spectra

were obtained at radiation intensities between 9.25×10^9 and 5×10^{10} W/cm², without and with He and Ar as carrier gases. Figure 1 shows the typical spectra. The most abundant detected m/q signals were 1, 12, 13, 16, 17, 18, 28, 29, 30, 32, 45 and 46 most of them corresponding to the breakdown of each of the molecular bonds of formic acid proposed previously for various authors using different types of projectiles. In Figure 1 the mass spectra as a function of the carrier gas are shown. The parent ion was only observed when not carrier gas was used, indicating that carrier gases inhibit the molecular ion formation. The results of the yield of the observed ions are listed on Table 1 for laser intensity of 4.32×10^{10} W/cm² along with the reported in previous papers (see references in the table)

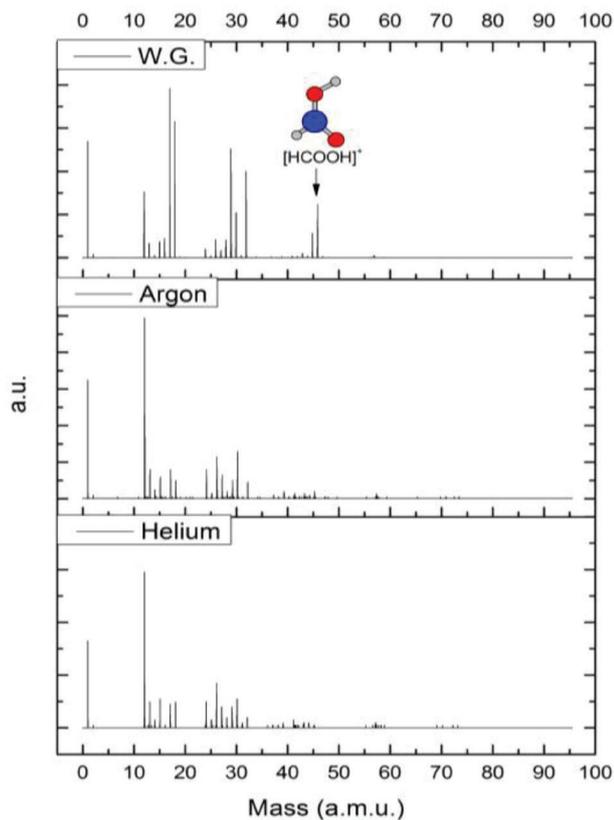


Figure 1: Formic Acid spectra at 4.33×10^{10} W/cm² without carrier gas (w.g.) and with Argon and Helium, in arbitrary units.

Table 1: Ionic Yield at 4.32×10^{10} W/cm².

amu	Ion	No gas	Carrier Gas		References
			Argon	Helium	
1	H ⁺	0.111	0.138	0.177	19, 21, 22
12	C ⁺	0.086	0.320	0.177	21, 23

13	CH ⁺	0.018	0.053	0.060	19, 21, 23
16	O ⁺	0.020	0.002	0.003	21,22
17	OH ⁺	0.164	0.036	0.044	10, 19, 21, 22
18	H ₂ O ⁺	0.129	0.027	0.049	19, 21, 22
28	CO ⁺	0.022	0.009	0.015	19, 21, 22, 23
29	CHO ⁺	0.135	0.027	0.046	10, 23, 21
30	COH ₂ ⁺	0.052	0.086	0.061	29, 22
32	O ₂ ⁺	0.080	0.011	0.018	19, 21
45	CO ₂ H ⁺	0.030	0.005	0.005	10, 19, 21, 22
46	CO ₂ H ₂ ⁺	0.058	---	---	19, 22

Ions with masses greater than the molecular ion, were also detected, indicating the presence of clusters predicted theoretically and reported before [23, 24]. Particularly masses 47 and 48, were also observed corresponding to protonated cation [24] HCOOH + H⁺ and HCOOH + H₂⁺. The intensity of ions with greater masses detected, increased as a function of the laser intensity. Regarding the ion CO₂H⁺ it is only observed in [22] in dissociation by electrons in [29]. It has not been experimentally reported in other papers. In Table 1 are displayed the different ions and the ionic yield at 4.32×10^{10} W/cm² from the present experiments along with the ions observed under different conditions and projectiles.

Most of the ion production increases with the laser intensity as it is shown in Figure 2 for some of the more abundant ions.

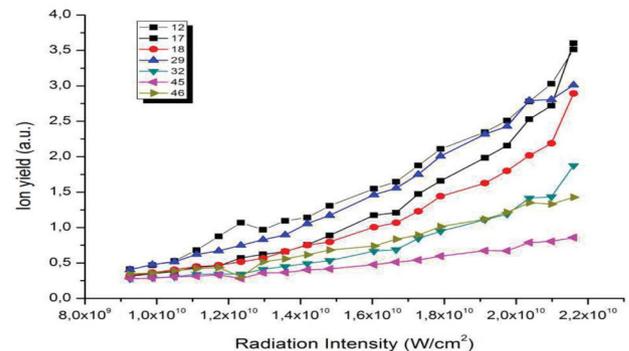


Figure 2: Ion yields, a.u., for more abundant detected masses [amu], as function of the radiation intensity, $9.25 \times 10^9 - 2.16 \times 10^{10}$ W/cm².

In the present study for all cases, regardless of the carrier gas, or its absence, the CO/CO₂ ratio was between 6 and 12. This is consistent with the existence of a mayor amount of *trans*-formic acid in which the dissociation channel

$\text{HCOOH} \rightarrow \text{CO} + \text{H}_2\text{O}$ is predominant over $\text{HCOOH} \rightarrow \text{CO}_2 + \text{H}_2$ considering a conformational memory [12-14]. This behavior is being discussed in different reports however the dependence on the multiphoton dissociation and intensity or carrier gases is not being reported before.

Conclusions

The multiphoton ionization spectroscopy is a technique which can comprise a wide range of highly sensitive experiments, for the study of the photon- molecule interaction processes when in the processes the system absorbs two or more photons, and absorption and emission are closely related, the simplest example of this type of experiment is when only absorption is involved. We present here some results based on the multiphoton ionization and dissociation of gas-phase formic acid. To our knowledge there are few experimental results on multiphoton processes related with the formic acid. This had allowed us to analyze the low mass positive ions as well as detect ions reported before, only produced by the interaction electrons with FA. From the comparison with former experiments, where different projectiles were used [photons, photons or electrons], there is still to prove what of the fragmentation paths contribute to the observed ions and to understand the response of such simple molecule to the projectiles. More experiments about the studies of these reactions and their influence on a vast area of research are needed [30]. Moreover [31] recent studies on dissociative electron attachment of formic acid show interesting dissociation pathways leading to negative hydrogen ions.

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