



## Infrared spectra of formic acid clusters in noble gas matrices



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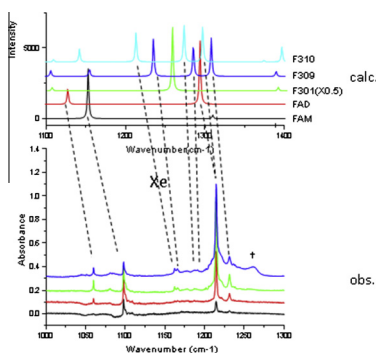
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### HIGHLIGHTS

- The first spectroscopic observation of formic acid clusters in noble gas matrices.
- DFT calculations of several possible isomers for trimer and tetramer.
- The observed clusters are assignable to two stable trimeric isomers.

### GRAPHICAL ABSTRACT

Observed vibrational peaks for formic acid clusters can be assigned to two stable isomers of  $(\text{HCOOH})_3$ , F309 and F310.



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### ABSTRACT

Infrared absorption spectra of formic acid clusters  $(\text{HCOOH})_n$  have been observed in noble gas matrices (Ar, Kr and Xe). The concentration dependence of the spectra and a comparison with the assigned monomeric/dimeric bands has led to the assignment of polymeric species  $(\text{HCOOH})_n$  ( $n > 2$ ). From comparisons of these spectra with several sets of DFT calculations, we concluded that the observed polymeric species can be assigned to stable isomers of  $(\text{HCOOH})_3$ .

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### Introduction

Molecular association of carboxylic acid molecules has been known for decades; it was proposed from the measurement of vapor density [1] for the first time. In the case of formic acid, the cyclic dimer (denoted as FAD hereafter) has been studied with electron diffraction techniques [2–4], and spectroscopic methods

[5–7] quite extensively. Other metastable dimeric species (open dimer) have also been observed in helium nanodroplets [8], and in noble gas matrices [5,9–11] in combination with infrared photo-excitation techniques. Experimental studies of larger clusters of formic acid  $(\text{HCOOH})_n$  ( $n > 2$ ), on the other hand, have been limited in mass spectrometry [12–14], and no spectroscopic observation has been reported to our knowledge. Since such species bridges the gap between FAD and formic acid in condensed phases, it is still an open question at what size formic acid cluster takes chain structure as in the bulk [15–17].

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In contrast to the current situation in the experimental works, theoretical investigations of larger formic acid clusters  $(\text{HCOOH})_n$  have been done up to  $n = 12$  [18–27]. In their serial studies using density functional theory (DFT), Thakkar et al. have obtained stable isomers for these larger clusters [21,22,25–27]. They showed that a chain-type hydrogen-bonded isomer is the most stable for  $n = 3$ , while  $\pi$ - $\pi$  interaction between two FAD moieties stabilizes isomers at  $n = 4$ . Results of vibrational calculations for these species have not been described in detail, however, and a comparison with experimental data has not been reported so far.

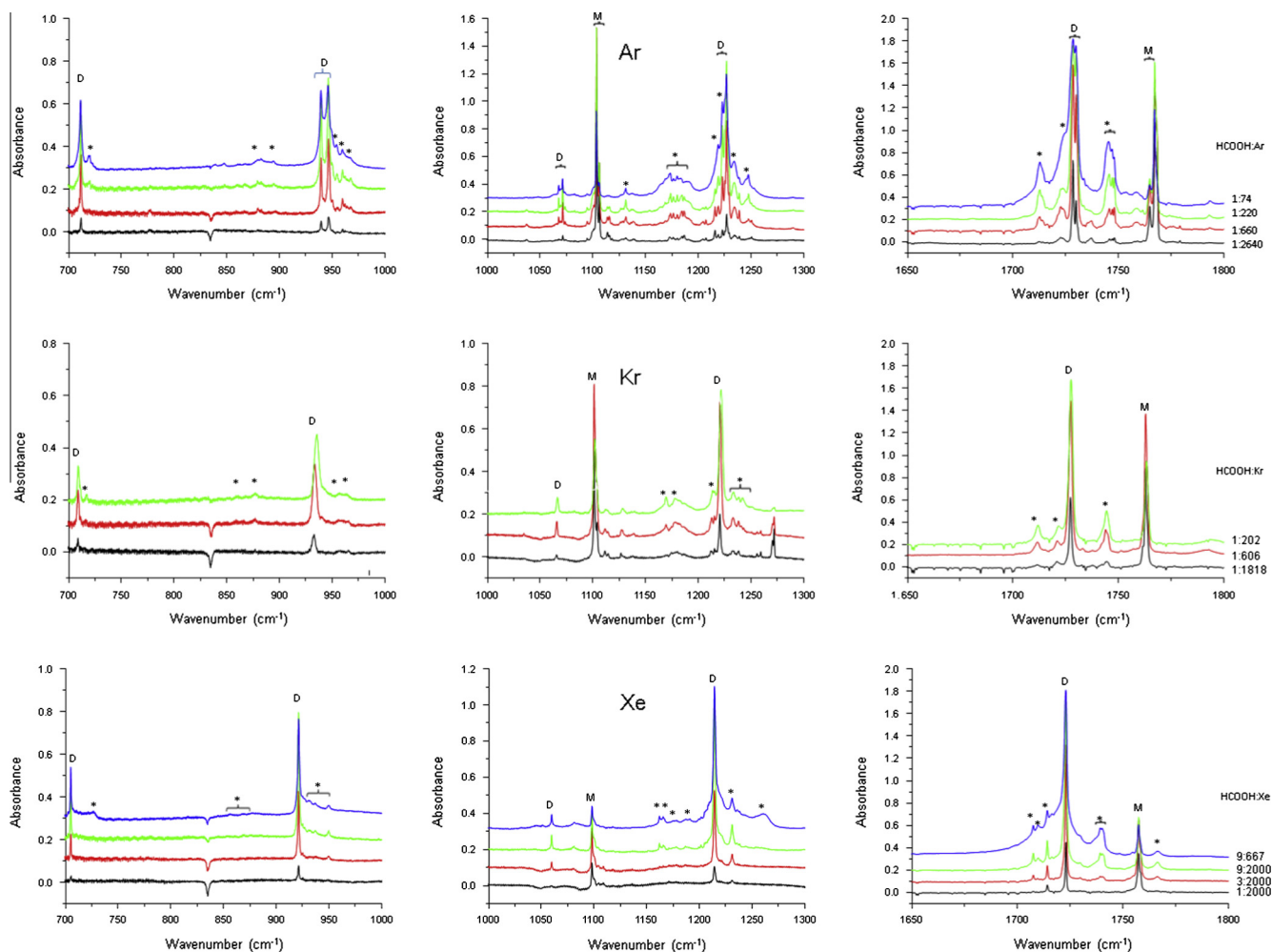
The aim of the present study is to provide spectroscopic data for the large formic acid clusters  $(\text{HCOOH})_n$  ( $n > 3$ ) by using matrix-isolation technique, and to compare them with theoretically simulated spectra for gaining structural information on these species, as has been done previously [28–34].

## Experimental

An experimental setup for the matrix-isolation spectroscopy has been described elsewhere [34] and will be briefly mentioned here. Premixed samples of formic acid vapor and noble gas were prepared in a stainless steel vessel, and they were expanded through a pulsed nozzle (General Valve, 0.8 mm $\phi$ ) and deposited onto a cold CsI substrate. The pulse width and the repetition rate were set to 450  $\mu\text{s}$  and 10 Hz, respectively. The deposition temperature was set to 20 K for Ar, 35 K for Kr and 45 K for Xe, in order

to minimize the scattering loss of incident light in the matrices. Infrared spectra of the matrix samples were measured with an FTIR spectrometer (JASCO FT/IR-6100) with the spectral resolution of 0.5  $\text{cm}^{-1}$  and the number of accumulation was typically 600.

Observed spectra in noble gas matrices are collected in Fig. 1. For clarity, spectra in Ar, Kr and Xe matrix are arranged in the top, middle and bottom traces, respectively. In each panel, the concentration dependence of the spectra is displayed from bottom to top. In reference to infrared spectra already reported [35–38], vibrational peaks for formic acid monomer (FAM) and dimer (FAD) were assigned and shown with the designations of M and D in the figure, respectively. Remaining bands, emerging with the increase of HCOOH concentration, were then assigned to polymeric species  $(\text{HCOOH})_n$  ( $n > 2$ ) and shown with the asterisks (\*) in each panel. As seen in Fig. 1, vibrational peaks in Ar matrix show notable splitting, especially for the dimeric bands, and those in Kr matrix are broadened. These features can also be observed for the polymeric bands, and it would be accounted for by multiple trapping sites, as previously [38]. On the other hand, vibrational peaks observed in Xe matrix are sharp and non-blended. Such difference due to the host environment has been observed for formic acid dimer [38] and  $\text{CHF}_2\text{Cl}$  [30]. Assigned vibrational peaks in the matrices are collected in Table 1. Each row includes corresponding peaks in the matrices, with the classification of band characteristics. The band designations for FAM and FAD are based on the Herzberg notations [39].



**Fig. 1.** Infrared spectra of formic acid clusters  $(\text{HCOOH})_n$  in noble gas matrices. Those in Ar, Kr and Xe are arranged in the top, middle and bottom traces. M and D denote monomeric bands and dimeric bands, respectively. Asterisks (\*) show polymeric bands ( $n > 2$ ), in view of concentration dependence of the spectra.

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