



Infrared and density functional theory studies of formic acid hydrate clusters in noble gas matrices



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ABSTRACT

Infrared absorption spectra of formic acid hydrate clusters $(\text{HCOOH})_m(\text{H}_2\text{O})_n$ have been measured in noble gas matrices (Ar and Kr). The concentration dependence of the spectra and the comparison with a previous experimental study on $\text{HCOOH}(\text{H}_2\text{O})$ and $\text{HCOOH}(\text{H}_2\text{O})_2$ [George et al., Spectrochim. Acta, Part A **60** (2004) 3225] led to the identification of large clusters. Density functional theory calculations at the B3LYP-DCP/6-31+G(2d,2p) level were carried out to determine the anharmonic vibrational properties of the clusters, enabling a consistent assignment of the observed vibrational peaks to specific clusters.

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1. Introduction

The microsolvation of acid molecules has attracted much attention in chemistry both from an experimental and theoretical point of view, due not only to its fundamental importance in the field, but also to its impact on environmental science. The microsolvation process can provide insights into the aerosol formation in the atmosphere, which contributes to radiative transfer processes and acid rain phenomena [1]. Particular interest has been directed to the hydration of formic acid, due to its relative simplicity and the high abundance of formic acid in the atmosphere [2].

In contrast to the numerous computational studies on formic acid hydrate clusters $(\text{HCOOH})_m(\text{H}_2\text{O})_n$ [3–12], experimental studies are still limited. The first spectroscopic observation of hydrate clusters in an Ar matrix was briefly described in Ref. [3]. Priem et al. observed some of these species in the gas phase by using Fourier transform microwave spectroscopy, and determined the rotational constants for $\text{HCOOH}(\text{H}_2\text{O})$, $\text{HCOOH}(\text{H}_2\text{O})_2$, and $(\text{HCOOH})_2(\text{H}_2\text{O})$ [13]. George and Sander published a matrix-isolation IR study of $\text{HCOOH}(\text{H}_2\text{O})$ and $\text{HCOOH}(\text{H}_2\text{O})_2$, combined with quantum chemical calculations [14]. Marushkevich et al. reported a hydration complex of *cis*-formic acid in Ar matrix [15]. Recently, Heinbuch et al. reported a mass spectrometry analysis of $(\text{HCOOH})_n$ and $(\text{HCOOH})_m(\text{H}_2\text{O})_n$ species in gas phase using soft X-

ray ionization techniques [16]; however, no structural information on the hydrates is available, in contrast to the case of larger carboxylic acid clusters [17,18]. It can thus be argued that formic acid hydrate clusters of moderate size have not been characterized experimentally.

In the present study, we report matrix-isolation infrared spectra of formic acid hydrate clusters. The spectra are compared with theoretical predictions from density functional theory (DFT) calculations to gain structural information on these species, following an approach successfully employed in the past [19–26].

2. Experimental

As previously done for trifluoroacetic acid [22], two sets of premixed samples of $\text{HCOOH}/\text{H}_2\text{O}/\text{Ng}$ (Ng = Ar, Kr) were used for the matrix-isolation experiments. One sample was obtained by mixing vapors of HCOOH , H_2O , and noble gas at various ratios (sample I), and another was prepared by mixing vapor from an aqueous solution of HCOOH ($\text{HCOOH}/\text{H}_2\text{O} = 1:1$ and $1:2$ volume ratio) with noble gases (sample II). The formic acid was purchased from Nacalai Tesque (Kyoto, Japan) and used after dehydration with anhydrous copper sulfate. Each liquid was degassed via freeze–pump–thaw cycles prior to the sample preparation.

Preliminary experiments with sample I did not reveal large HCOOH hydrate clusters: only the vibrational peaks of $\text{HCOOH}(\text{H}_2\text{O})$ and $\text{HCOOH}(\text{H}_2\text{O})_2$ could be assigned, based on the result of Ref. [14]. On the other hand, the analysis of sample II

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revealed additional vibrational peaks, which were apparently due to large hydrate clusters. Such spectral difference has been observed previously [22], and may result from the preferential formation of HCOOH hydrate clusters in the gas phase in equilibrium with the liquid samples. Therefore, only the results obtained with sample II will be presented in the next section. The premixed sample was deposited onto a cold CsI surface maintained at cryogenic temperature. The temperature of the substrate was set to 20 K for Ar and 35 K for Kr, in order to minimize the scattering loss of the incident light in the matrices. Other details of the experimental setup have been described elsewhere [26] and will not be repeated here.

The spectra obtained in the two matrices are shown in Fig. 1. In reference to the infrared spectra already reported [27–30], the absorption bands of formic acid monomer and dimer are labeled 'M' and 'D', respectively. The vibrational peaks of the HCOOH(H₂O) and HCOOH(H₂O)₂ complexes in the Ar matrix [14] are marked with daggers (†) and double daggers (‡), respectively. Additional peaks emerging with increasing sample concentration can be assigned to larger hydrates, and are designated with asterisks (*). The corresponding peaks in the Kr matrix are marked in the same way. The absorption bands of formic acid polymers [26] could not be assigned, due to the preferential formation of hydrate clusters with sample II. As also seen in the figure, the vibrational peaks of the hydrate clusters in the Kr matrix are sharper than in Ar, an effect that could be associated to multiple trapping sites in Ar [30]. The vibrational wavenumbers corresponding to each peak are collected in Table 1. At this stage, the assignment of the peaks associated to a specific (HCOOH)_m(H₂O)_n hydrate cluster remained unclear. One possibility would involve assigning the peak at 1184 cm⁻¹ in Ar (1186 cm⁻¹ in Kr) to HCOOH(H₂O)₂, in view of the sequential red-shift from the corresponding monomer band. The discrepancy between theoretical and experimental results, however, seems too large: the frequency shift from the monomer band for this peak was +84 cm⁻¹ in Ref. [14] and that for the HCOOH(H₂O)₂ complex was calculated to be +119 cm⁻¹ at the MP2/

6-31++G(d,p) level. For a more definitive assignment, therefore, the observed peak positions were compared with the results of vibrational calculations with anharmonic corrections, which will be described in the following sections.

3. Calculations

All calculations for formic acid hydrate clusters (HCOOH)_m(H₂O)_n ($m = 1, 2; n = 0-4$) were done with the GAUSSIAN 09 [31] package. Two sets of DFT calculations were carried out for these clusters: the first employing the Coulomb-attenuating method/three-parameter Becke-Lee-Yang-Parr (CAM-B3LYP) functional [32] with the 6-31++G(3df,3pd) basis set, and the second based on the B3LYP functional with dispersion-correcting potentials (B3LYP-DCP) with the 6-31+G(2d,2p) basis set [33,34]. The B3LYP-DCP method has been proven to give a better description of non-covalent interactions compared to almost all other DFT-based methods [33]. Additional calculations were also carried out at the MP2/6-31++G(3df,3pd) level.

The initial structures for each hydrate cluster shown in Fig. 2 were constructed by taking into account previous experimental studies [13,14] and the extensive work of Nordstrom et al. [11]. It was assumed that the isomeric structures observed experimentally are global minima. In the following, the designation (m,n) stands for the hydrate cluster (HCOOH)_m(H₂O)_n. Ring-type structures were also considered for the trihydrate (1,3) and two isomers of tetrahydrate (1,4) in analogy with trifluoroacetic acid (TFA) hydrates [22,35,36]. Following structure optimization, each cluster was subjected to a vibrational frequency calculation to confirm that an energy minimum had been reached.

All the structures in Fig. 2 were converged to energy minima. As in the case of TFA-(H₂O)₄ clusters [35], the bicyclic [2 + 2]2d isomer is more stable than the cyclic [4 + 0] one. The corresponding energy difference $E([2 + 2]2d) - E([4 + 0])$, varies with the level of calculation: -455 and -602 cm⁻¹ at the CAM-B3LYP/6-31++G(3df,3pd) and B3LYP-DCP/6-31+G(2d,2p) levels,

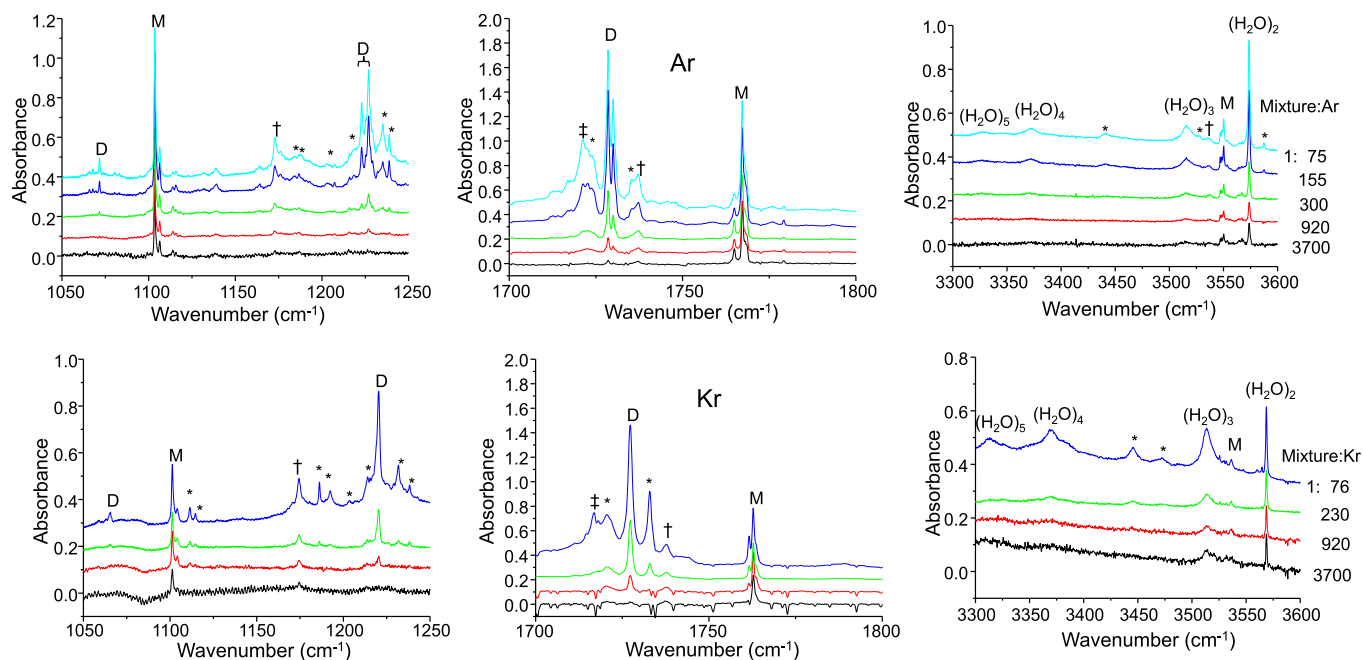


Fig. 1. Infrared spectra of formic acid hydrate clusters in noble gas matrices. M and D denote monomeric and dimeric bands, respectively, whereas † and ‡ represent HCOOH(H₂O) and HCOOH(H₂O)₂ complexes assigned from Ref. [14]. Other hydrate clusters are marked with asterisks (*). Absorption peaks of water clusters (H₂O)_n in the O–H stretching region were assigned from Ref. [44].

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