

# The acetylacetonone-water complex in a low-temperature solid argon matrix



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## ABSTRACT

A mixture of acetylacetonone and water was condensed in low-temperature Ar matrices at 5 K, and infrared spectra were observed. It was found that the H<sub>2</sub>O molecules formed hydrogen bonds with the acetylacetonone. The structure of the H<sub>2</sub>O-C<sub>5</sub>H<sub>8</sub>O<sub>2</sub> complex was estimated with the aid of a density functional calculation. A similar sample was prepared using deuterium-substituted water to confirm the structure of the complex. Upon annealing the matrix-isolated sample, aggregation of H<sub>2</sub>O molecules was observed and the amount of the complex remained unchanged.

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## 1. Introduction

Acetylacetonone (C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>, AA) is a simple β-diketone that is commonly applied as a ligand of organometallic compounds. It is well known that the AA molecule has two tautomers (keto and enol forms), and the enol tautomer is more stable in the gas phase because of an intramolecular hydrogen bond associated with π-electron delocalization over the O=C–C=C–O–H ring. On the other hand, the keto form is more stable in polar solvents, especially hydrogen-bonding solvents such as water [1]. Furthermore, a theoretical study of the catalytic effect of water molecules on the keto-enol tautomerism has been reported [2]. However, to the best of our knowledge, no experimental study on hydrogen bonding between AA and water molecules using a matrix isolation technique has yet been reported.

Photoisomerization of AA isolated in low-temperature argon matrices has been reported. UV irradiation (λ > 280 nm) induced the production of various enol isomers by cis-trans isomerization around C–C and C=O bonds [3]. The enol conformer of AA was also produced by UV irradiation at 266 nm in nitrogen [4] and parahydrogen [5] matrices. Furthermore, UV irradiation with a shorter wavelength (λ < 280 nm) induced keto tautomerization [6]. Infrared spectra of the AA isomers have been well investigated, and it is easy to assign the conformations of the AA molecule.

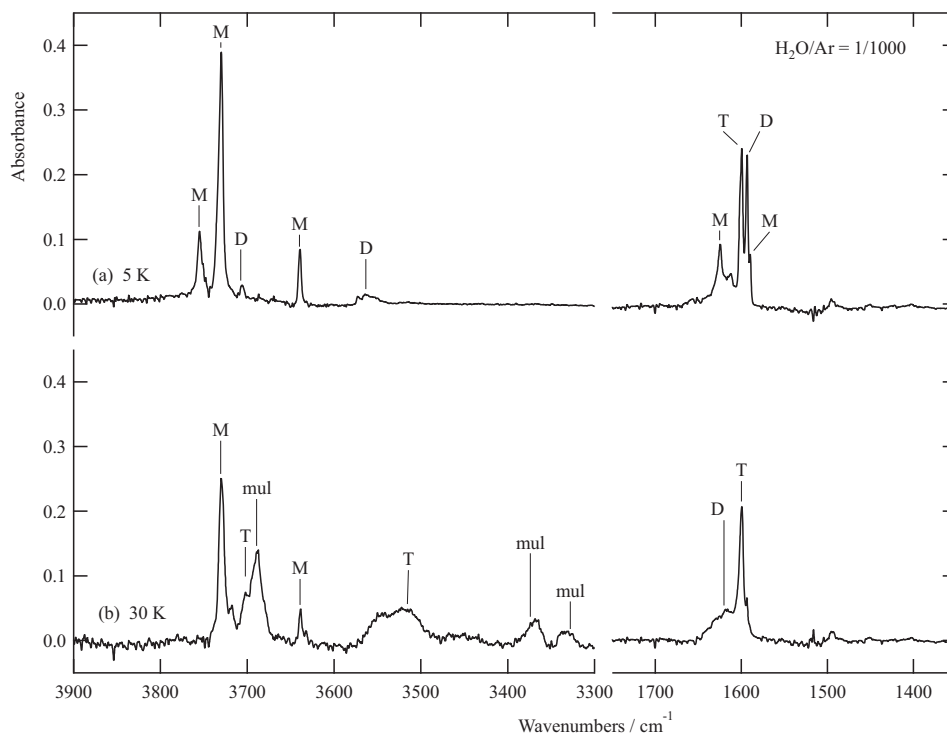
Infrared spectra of a water molecule and clusters have been studied extensively by many groups [7–16], and the assignments are summarized in the literature [17]. The infrared spectra of water in low-temperature matrices are complicated because of the existence of rotating and non-rotating monomers, and coexistence of different molecules in a matrix increases the number of non-rotating monomers. Meanwhile, hydrogen bonding between water molecules and other simple molecules has attracted considerable attention. Hydrogen bonding with formic acid produced cyclic HCOOH–H<sub>2</sub>O complexes [18]. A hypoxanthine–water complex [19] and an acetylene–water complex [20] were studied using a matrix-isolation technique. A dimethyl ether–water complex [21] and an acetone–water complex [22,23] were studied, and the red-shifts of both ν<sub>1</sub> and ν<sub>3</sub> of H<sub>2</sub>O molecule were observed. Studies on hydrogen bonding between water and simple organic molecules provide useful information on the nature of solvation.

## 2. Experimental

AA from Kanto Chemical Co., Inc. (99.5%) and water (H<sub>2</sub>O and D<sub>2</sub>O) were degassed prior to use. Ar gas (99.9999%) was purchased from Taiyo Nippon Sanso. Gas mixtures with various AA/H<sub>2</sub>O/Ar ratios prepared in a gas line were deposited onto a CsI substrate cooled to 5 K using a closed-cycle He cryostat (RDK205D, Sumitomo Heavy Industries, Ltd.). The temperature of the sample was controlled at the desired temperature using a temperature controller (Model 9700, Scientific Instruments), and the deposition rate (0.5–0.9 sccm) was controlled by a needle valve. Fourier

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**Fig. 1.** Infrared spectra of H<sub>2</sub>O in an Ar matrix, H<sub>2</sub>O/Ar = 1/1000, measured at (a) 5 K and (b) 30 K. The marks M, D, T, and mul in the figure denote the H<sub>2</sub>O monomer, dimer, trimer, and multimer, respectively.

transform-infrared (FT-IR) spectra were measured using a Perkin Elmer System 2000 spectrometer. Density functional calculations were performed using the Gaussian09 and GaussView5 programs [24].

### 3. Results and discussion

#### 3.1. H<sub>2</sub>O and AA in an Ar matrix

First, an infrared spectrum of water H<sub>2</sub>O (Fig. 1a) isolated in an Ar matrix was measured at 5 K without mixing with AA. The H<sub>2</sub>O/Ar = 1/1000 spectrum (Fig. 1a) was in good agreement with the spectrum reported in the literature [17]. Matrix-isolated water exhibits many bands due to non-rotating and rotating monomers, and the peaks are strongly affected by matrix effects: materials of the matrices, concentration, deposition conditions, and annealing [7,14,15]. The absorption at 3730 cm<sup>-1</sup> was assigned to the asymmetric stretching mode  $\nu_3$  of the non-rotating monomer, and the absorption at 3756 cm<sup>-1</sup> was assigned to a quasi-freely rotating monomer ( $0_0 \rightarrow 1_{-1}$ ) [12,17]. Symmetric stretching mode  $\nu_1$  and bending mode  $\nu_2$  appeared at 3639 and 1590 cm<sup>-1</sup>, respectively. In addition to the bands assigned to the monomer H<sub>2</sub>O, several weak peaks were observed: peaks at 3707, 3574 and 1594 cm<sup>-1</sup> were assigned to a dimer (H<sub>2</sub>O)<sub>2</sub>, and a peak at 1602 cm<sup>-1</sup> was assigned to a trimer (H<sub>2</sub>O)<sub>3</sub>. The temperature of the sample was increased to 30 K (Fig. 1b), and this change in temperature was completed within 5 min. The temperature of the sample was kept at 30 K for 2 h, and the shape of the spectrum remained unchanged. The aggregation of H<sub>2</sub>O molecules was completed during first 5 min at 30 K. The multimer (H<sub>2</sub>O)<sub>n</sub> peaks at 3690, 3370, 3331 cm<sup>-1</sup> and the trimer (H<sub>2</sub>O)<sub>3</sub> peak at 3516 cm<sup>-1</sup> appeared with a decrease of monomer and dimer peaks.

The infrared spectrum for AA/Ar = 1/1000 was measured at 5 K (Figs. 2a and 3a), and was exactly the same as that reported in the literature [3,25]. No peak of AA was observed in the region

between 3900 and 3300 cm<sup>-1</sup> (Fig. 2a). The AA has absorptions at 1635 and 1616 cm<sup>-1</sup> (Fig. 3a), which are the C=C stretching and the C=O stretching mode associated with O–H bending, respectively. The most stable isomer of the enol form was obtained in the spectrum, while the trace amount of keto form was observed at 1711 cm<sup>-1</sup> [3]. The assignments of the IR peaks [17,25] are listed in Tables 1 and 2.

#### 3.2. Co-condensation of H<sub>2</sub>O and AA in an Ar matrix

In order to investigate the interaction between AA and H<sub>2</sub>O, infrared spectra of samples produced by condensation of gas mixtures of AA/H<sub>2</sub>O/Ar were measured at 5 K varying the mixture ratio; AA/H<sub>2</sub>O/Ar = 1/1/1000 (Figs. 2b and 3b), 1/3/1000 (Figs. 2c and 3c), and 1/10/1000 (Figs. 2d and 3d). In the spectra in a region between 3900 and 3300 cm<sup>-1</sup> (Fig. 2), most of the peaks were assigned to H<sub>2</sub>O molecules. At the lowest H<sub>2</sub>O concentration (Fig. 2b), the non-rotating H<sub>2</sub>O monomer at 3730 cm<sup>-1</sup> and the dimer at 3707 cm<sup>-1</sup> were observed. With increasing the concentration of H<sub>2</sub>O (Fig. 2c and d), the peaks of dimers, trimers, and multimers increased. It was found that H<sub>2</sub>O molecules readily aggregate in a mixture of AA/H<sub>2</sub>O/Ar because of the increase in lattice defects produced by the AA molecules. The peak of the rotating H<sub>2</sub>O monomer at 3754 cm<sup>-1</sup> also enhanced because of the lattice defects in a mixture of AA/H<sub>2</sub>O/Ar. The peak at 3780 cm<sup>-1</sup> was assigned to the H<sub>2</sub>O monomer ( $\nu_3$ ;  $1_{-1} \rightarrow 1_{-2}$ ), though it had a 4-cm<sup>-1</sup> higher value than that reported in the literature [17]. Though this peak was not observed in the H<sub>2</sub>O/Ar spectra (Fig. 1), this rotation H<sub>2</sub>O monomer at 3780 cm<sup>-1</sup> appeared because of the lattice defects in an AA/H<sub>2</sub>O/Ar mixture. Whereas most of the peaks were associated with H<sub>2</sub>O, new peak at 3496 cm<sup>-1</sup> (marked in red in Fig. 2) was not assigned to any previously reported species, and was obviously due to interactions between H<sub>2</sub>O and AA molecules: a H atom in H<sub>2</sub>O hydrogen bonded to one of the O atoms in AA. The H<sub>2</sub>O-AA complex was speculated to have the structure indicated in

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