Pressure-dependent studies on hydration of the C–H group in formic acid

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The infrared spectroscopic profiles of HCOOD/D_2O mixtures were measured as a function of pressure and concentration. The C–H bond of HCOOD shortens as the pressure is elevated, while the increase in C–H bond length upon diluting HCOOD with D_2O was observed. Based on the experimental results, the shift in frequency of C–H stretching band is concluded to relate to the mechanism of the hydration of the C–H group and the water structure in the vicinity of the C–H group. The pressure-dependent results can be attributed to the strengthening of C–H---O electrostatic/dispersion interaction upon increasing pressure. The observations are in accord with *ab initio* calculation forecasting a blueshift of the C–H stretching mode via C–H---O interaction in HCOOD-water/$(HCOOD)_2$-(D_2O) complexes relative to the noninteracting monomer/dimer. Hydrogen-bonding nonadditivity and the size of water clusters are suggested to be responsible to cause the redshift in C–H stretching mode upon dilution HCOOD with D_2O. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1409363]

I. INTRODUCTION

The properties of water have a large bearing on biological systems and are related to the highly associating nature of water through its ability to form hydrogen bonds.[1,2] Adding to the scientific interest in water is its poor ability to solvate nonpolar functional groups, i.e., the hydrophobic effect.[3,4] C–H---O interaction[5,6] has been the subject of experimental and theoretical studies and formic acid is one of the model systems to investigate such weak hydrogen-bonding interaction. We shall restrict our attention in this article to binary mixtures of water with formic acid.

Formic acid molecules can be expected to act as proton donors because of the low pKa values. Furthermore, they are able to accept a proton via their C=O group and form a second hydrogen bond. It is well known[7–11] that formic acid molecules are hydrogen-bonded pairwise to form cyclic centro-symmetric dimers in the gas phase. Whether the structure of liquid formic acid should be described as a collection of cyclic dimers has been the subject of controversy for a long time.[8–14] Several infrared and Raman investigations show the existence of cyclic dimers and the chainlike polymer structure in the liquid state.[12,13] Nevertheless, based on the results of Raman spectral study, Bartholomew and Irish[14] concluded that liquid formic acid should be viewed as a collection of monomeric units which interact through hydrogen bonding, thereby imposing local, short-term order in the liquid. Other workers[8] also suggested that the role of the cyclic dimers, characteristic of the gas phase with two O–H---O hydrogen bonds, is minor (7% of the molecules) in the liquid formic acid. The formic acid dimer in the gas phase[7–11] and the long chains in the crystals[15–20] show the variety of hydrogen bonds which formic acid can form. Knowledge of the microscopic details of neat formic acid has been greatly enhanced in the literature,[9–13] while experimental evidence of C–H---O interaction among formic acid cluster has been difficult to obtain. Several theoretical investigations suggested the existence of the C–H hydrogen-bonding dimers[7,11,21] in the gas phase. The aim of this paper is to show how the pressure-dependent variations in the mid-infrared spectra of HCOOD/D_2O are correlated to structural information.[22]

One of the central issues in understanding the hydration of C–H group is the frequency shift upon dilution with water. As we know, the vibrational modes undergo a red frequency shift and accompany intensification upon formation of the hydrogen bond in most strong hydrogen bonded systems via N–H---O or O–H---O interactions.[5] While diluting with water, the C–H bond suffers a precisely opposite change, i.e., blueshift of vibrational frequency, in many liquids.[3–5] Mizuno *et al.*[3,4] proposed that the interactions between the C–H hydrogen and water oxygen are repulsive, so that a part of the electron about the C–H proton is pushed out into the C–H bond due to the repulsive force. To ratio-

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nalize the experimental observations, it has also been reported that the in-plane lone pair electrons of carbonyl oxygen in aldehydes give an antibonding contribution to the C–H bond.[5,23] When these electrons are engaged in hydrogen bonding, their antibonding contribution is known to diminish, resulting in the blueshift of the C–H stretching mode. However, the infrared spectral feature in the CH_3 asymmetric stretching region for the acetone/methanol-d_4 becomes asymmetric toward its low-frequency side upon the increase of methanol-d_4 concentration.[24] The new spectral feature in the low-frequency side may be assumed to arise from interactions between acetone and methanol via C–H---O. Furthermore, in *ab initio* calculation, the CH_3 stretching band of acetone is computed to redshift by 3.5 cm^{-1} upon forming the acetone/methanol binary complex.[24] The controversy arises mainly because of the difficulty in observing the perturbed C–H band due to the inherent weakness of C–H---O interaction. The C–H---O interaction is typically weak or less than 4 kJ/mol. Nevertheless, strengths of the C–H---O interactions can be enhanced in protonated clusters or molecular aggregates containing charges. Recent studies also showed that the hydrogen-bonded C–H---O interaction is more predominant in high-pressure ices than van der Waal interaction.[25] The cooperative effects of hydrogen bonds and the bond angles of water clusters may be likely to cause the transition from the van der Waal-type interaction to C–H---O hydrogen bond formation.[25] We hope our high-pressure study on aqueous formic acid solutions will help us to be clear about the speculative nature of C–H---O interactions.

The use of pressure as a variable for studying biological related molecules is a field that is developing rapidly. In addition to being an important thermodynamic variable, pressure can be used as a valuable means of triggering and investigating the folding and unfolding transition of large molecules such as polymers or proteins. Compared to varying temperature, which produces simultaneous changes in density (or volume) and thermal energy, the use of pressure perturbs the environment of the target molecules in a continuous, controlled way by changing intermolecular distances. On the basis of the results of high-pressure FTIR measurements using diamond anvil cell (DAC) up to the pressure of 3 GPa,[25,26] we will explore the hydration mechanism of the C–H group in HCOOD/D_2O mixtures.

II. EXPERIMENT

Samples of HCOOD/D_2O mixtures were prepared using 98% HCOOD supplied by Aldrich and 99.97% D_2O supplied by Merck. A diamond anvil cell (DAC) of Merril-Bassett design, with a diamond culet size of 0.6 mm, was used for generating pressures to approximately 3 GPa. Two type IIa diamonds were used for mid-infrared measurements. The samples were contained in 0.3 mm-diameter holes in 0.25 mm-thick stainless-steel gaskets mounted on the diamond anvil cell. To reduce the absorbance of the samples, CaF_2 powder was placed into the holes and was compressed firmly before the samples were put in. Then a droplet of samples filled the empty space of the entire hole of the gasket in the DAC and was subsequently sealed when the opposed anvils

were pushed toward each other. Infrared spectra of the samples were measured on a Perkin Elmer Fourier transform spectrophotometer (model Spectrum RXI) with a LITA (lithium tantalate) mid-infrared detector. The infrared beam was condensed by a 5X beam condenser manufactured by Perkin-Elmer onto the sample in the diamond anvil cell. Typically a resolution of 4 cm^{-1} was chosen (data point resolution of 2 cm^{-1}). For each spectrum typically 1000 scans were co-added. To remove the absorption of diamond anvils and CaF_2, the absorption spectra of DAC with gaskets filled with CaF_2 were measured first and subtracted from those of the samples. The interference from D_2O is not negligible for mole fraction of HCOOD<0.1 (data not shown), so the absorption spectra of DAC with gaskets filled with D_2O and CaF_2 were measured under various pressures first and subtracted from those of the samples.[25]

Samples measured at ambient pressure were taken by filling the samples in a cell with two ZnSe windows without spacers (thickness of samples <100 μm). The spectra of D_2O were subtracted from those of the samples.

III. RESULTS AND DISCUSSION

The spectrum of neat HCOOD shows the C=O stretching vibrations locating at ~1717 cm^{-1} and the C–H stretching vibration at ~2944 cm^{-1}, respectively. The C–H stretching of HCOOD overlaps with the OH stretching bands of H_2O and HCOOH molecules, locating at similar positions, so C–H stretching vibrations for HCOOD in the solution of D_2O instead of HCOOH/H_2O were studied in this article. As shown by Fig. 1, where band frequency of C–H stretch [Fig. 1(a)] and carbonyl [Fig. 1(b)] vibrations have been plotted versus mole fraction of HCOOD, the decrease of C–H and C=O stretching frequency upon dilution with D_2O were observed. The redshifts in C=O are attributed to hydrogen-bonding interaction of the C=O with the OD group of D_2O, since the deuterium atom of D_2O was assumed to point toward the carbonyl oxygen. The redshift of C–H stretching frequency and bandwidth variation upon dilution HCOOD with D_2O are totally different from other molecules.[3–5,27,28] The blueshifts with dilution were observed in C–H stretching frequency in acetone,[27] dimethyl sulfoxide (DMSO),[3] ethanol[28] and tert-butyl alcohol.[4] The system of diluted HCOOD in D_2O is considerably simpler than neat HCOOD concerning the study of the C–H stretching because the coupling between various C–H among HCOOD molecules is greatly decreased. The width of C–H mode is as much as 47 cm^{-1} in the neat HCOOD and remains as 53 cm^{-1} in diluted HCOOD (mole fraction of HCOOD=0.24). Based on the experimental results, the C–H---O interaction may be a distinct possibility to understand the redshift and spectral profiles of the C–H stretching mode in diluted HCOOD mixtures. This may be a response to the formation of C–H---O interaction connecting the D_2O molecules and the HCOOD oligomers, replacing the C–H---O interaction among HCOOD molecules.

In order to learn the molecular structure of neat HCOOD and HCOOD/D_2O mixtures, the pressure study seems to of-
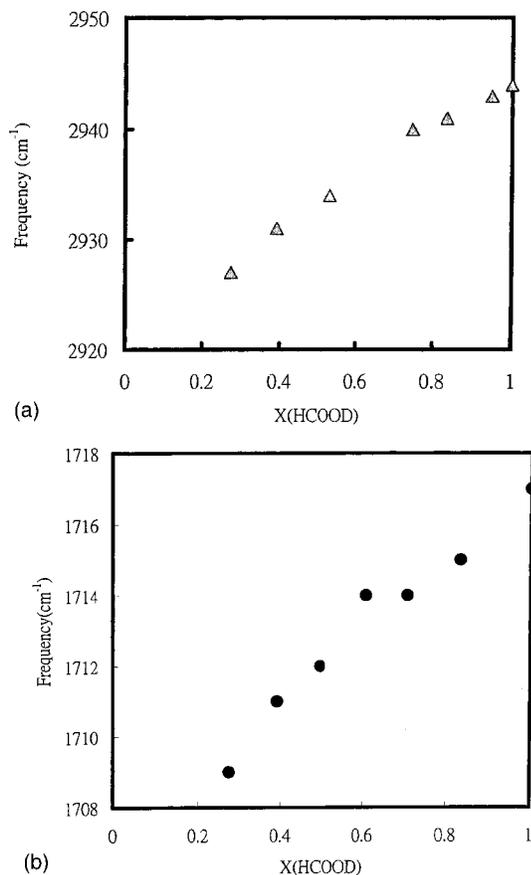
FIG. 1. (a) Concentration dependence of the C–H stretching frequency of HCOOD/D_2O vs the mole fraction of HCOOD. (b) Concentration dependence of the C=O stretching frequency of HCOOD/D_2O vs the mole fraction of HCOOD.
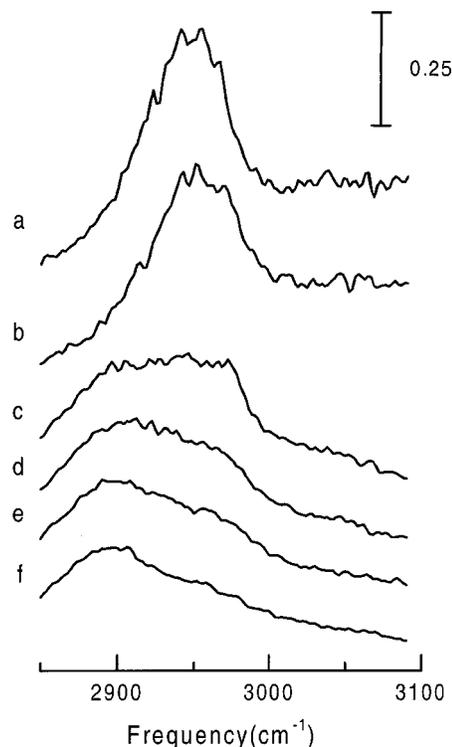

FIG. 2. IR spectra in the region of C–H stretching of neat HCOOD under the pressure of (a) ambient, (b) 0.3 GPa, (c) 0.9 GPa, (d) 1.5 GPa, (e) 1.9 GPa, and (f) 2.3 GPa, respectively.

fer the direct approach. Figure 2 illustrates the experimental mid-infrared spectra of neat HCOOD in the region of C–H stretching mode obtained in terms of absorbance at room temperature under ambient pressure (curve a), 0.3 GPa (curve b), 0.9 GPa (curve c), 1.5 GPa (curve d), 1.9 GPa (curve e), and 2.3 GPa (curve f), respectively. In the liquid phase region ($P<0.8$ GPa, curve a and b), the C–H stretching frequency increases gently upon pressure increased and this corresponds to the contraction of the C–H bond. A phase transition was observed at pressure >0.8 GPa,[29] i.e., curve c-f, while the IR spectra of C-H stretching mode consist of at least two bands overlapping each other in curve c-f. These two bands become well-separated in the derivative spectra. We anticipate that the low frequency component is attributed to the creation of a hydrogen bond between neighboring molecules or adjacent chains,[20,29] so that a hydrogen-bonded network is formed. Formic acid and acetic acid are known to form low-temperature crystal characterized by infinite hydrogen-bonded chains tightly packed in layers, while all the other molecules among the monocarboxylic acid series form isolated dimer pairs linked by weak intermolecular bonding.[15–18,29] Although the structural properties of formic acid in low-temperature crystalline form are understood, controversial conclusions about the configuration of formic acid in high-pressure crystalline form ($P>0.8$ GPa) still remain. Recently Allan *et al.*[29] found the high-pressure crystal structure of formic acid is quite different from that formed at low temperature.[16–18] Formic acid molecules adopt both the cis and trans conformation in the high-pressure structure,[29] while only trans molecules are formed in the low-temperature structure.[16–18,20]

Figure 3 shows the IR spectra of a HCOOD/D_2O mixture with mole fraction of HCOOD equal to 0.24 under pressure in the order of increasing pressure, revealing only one Gaussian-like band in the region of C–H stretching vibration. It should be noted first that the frequency of the C–H stretching mode which characterizes the C–H---OD_2 interactions increases with increasing pressure with a slope ($d\nu/dP$) of 8 cm^{-1}/GPa. This behavior contrasts with the general trend of a redshift with pressure for O–H and C=O stretching mode in strong hydrogen-bonded systems via O–H---O and C=O---H, respectively. The increase in frequency of the C–H stretching mode is a result of the decrease in the C–H bond length. The possible explanation is that the C–H hydrogen is pushed toward the carbon by water oxygen due to modification of the hydrogen-bond network by varying the pressure.[3,4] In the case of water, it has been shown that the hydrogen-bond network can be modified by varying the pressure.[30] Thus, the blueshift should be closely related to the mechanism of the hydration of the C–H group and the water structure in the vicinity of the C–H group. Mizuno *et al.* observed that the vibration frequencies of the C–H stretching mode of acetone,[27] DMSO,[3] and tert-butyl alcohol[4] show an increase with increasing water concentration. To the elucidation of the blueshifts of the C–H band, the electronic repulsion and/or dispersion interaction between the hydrogen and water oxygen atoms, i.e., the push-
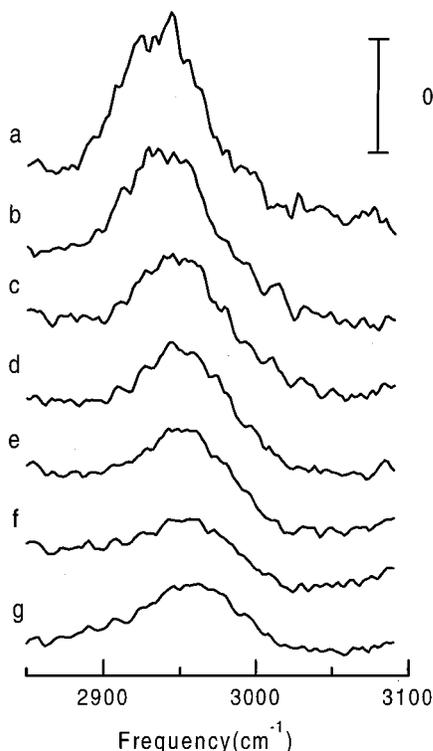
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FIG. 3. Pressure dependence of the C–H stretching in a HCOOD/D$_2$O mixture with mole fraction of HCOOD equal to 0.24 in the following condition: (a) ambient, (b) 0.3 GPa, (c) 0.9 GPa, (d) 1.5 GPa, (e) 1.9 GPa, (f) 2.3 GPa, and (g) 2.5 GPa, respectively.

ball hydration mechanism, were proposed in their works.[3–4] Interestingly enough, the pushing effect seems to be tunable or enhanced via pressure in the HCOOD/D$_2$O mixture, while our experimental results demonstrated the blueshift of C–H stretching vibration versus pressure.

The concentration dependence of the C–H mode, obtained from mixtures of X(HCOOD)=0.75, 0.53 and 0.24, respectively, was plotted as Fig. 4, showing the trend of blueshift with pressure. To determine the correct band center, the peak in the region of 2920–3000 cm^{-1} was analyzed by fitting a Gaussian function.[31] The concentration-dependent
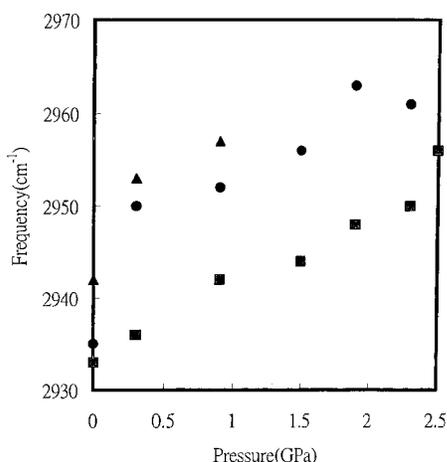

FIG. 4. Pressure dependence of the C–H stretching in HCOOD/D$_2$O mixtures with mole fraction of HCOOD equal to 0.75 (triangle), 0.53 (circle), and 0.24 (square), respectively.

results in Fig. 4 indicate that (formic acid)$_x$(water)$_y$ complexes with $x, y \geq 1$ display contraction of the C–H bond length and positive frequency shift of the C–H stretching modes as the pressure was elevated. Turi[7] illustrated that C–H---O hydrogen-bonds play a significant role in determining the liquid dynamics in formic acid, while the C–H hydrogen-bonding formic acid dimer displays a positive frequency shift of the C–H stretching mode relative to the noninteracting monomer. Their results[7] indicated that weak C–H---O interaction, displaying a blueshift in frequency, is a great contrast to the other strong hydrogen-bondings via O–H---O or N–H---O, revealing a redshift in frequency upon the formation of hydrogen bonds. The pressure seems to have dominant influence to enhance the C–H---O interactions for formic acid-formic acid and formic acid-water complexes, since the blueshifts in frequency were observed for various HCOOD/D$_2$O concentrations in Fig. 4. The origin of the C–H bond-shortening upon forming a weak hydrogen bond has been the subject of numerous discussions.[3–5] At small electric fields, the C–H bond of methane-water complex shortens as the electric field increases until the field reaches 0.02 a.u. then lengthens as the field increases.[32] In light of the work of a methane-water systems,[32] the blueshift observed in Fig. 4 may be attributed to the strengthening of electrostatic C–H---O contacts due to compression. Thus, electron density from the hydrogen, being electron rich with respect to the carbon, moves into the C–H bond as the pressure increased as a result of the shortening of the C–H bond. Recently, several structures of complexes between formic acid and water were identified from measurements of rotational transitions, revealing ring structures with hydrogen bond(s).[21] In its most stable complex, (formic acid)$_2$-water forms a ten-membered ring structure by three O–H---O hydrogen bonds. In addition to the most stable (formic acid)$_2$-water complex, a stable conformer, where water is loosely attached to C–H via C–H---O in the plane of the formic acid dimer, was predicted by the *ab initio* calculation.[21] Thus the electric field induced by C–H---O interaction in formic acid/water may be small. The strengthening of C–H---O electrostatic contact caused by pressure and temperature on the crystalline acetone has been reported.[33]

To facilitate interpretation of the experimental spectra, *ab initio* calculations were carried out with the GAUSSIAN 94 program package[34] using density functional theory (DFT). We have adopted the B3LYP functional and employed the standard 6-31+G* basis set. The DFT/B3LYP method combined with such a basis set allows us to predict the geometry, binding energies, harmonic vibrational frequencies and infrared absorption intensities of various structural isomers to be compared with the experimental measurements. As shown in Fig. 5, we examined the frequencies of the C–H stretching modes of formic acid monomer associated with one water molecule [Fig. 5(a)], two water molecules [Fig. 5(b)], three water molecules [Fig. 5(c)], and four water molecules [Fig. 5(d)], respectively. A single factor (0.955) was used to scale the calculated frequencies.[25] The predicted C–H stretching frequencies are 2963, 2996, 2991, and 2969 cm^{-1}, corresponding to Figs. 5(a)–5(d), respectively. As illustrated in
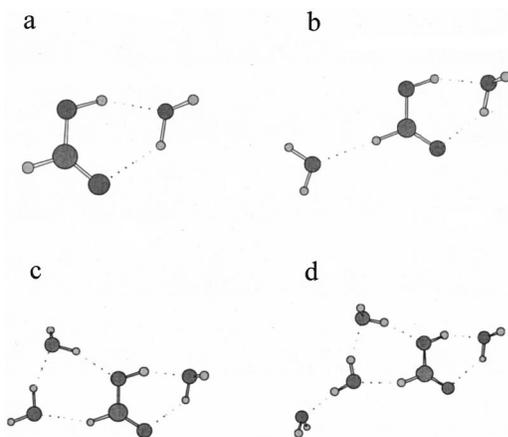
FIG. 5. Optimized structure of the (a) HCOOD-water complex, (b) HCOOD-(water)$_2$ complex, and (c) HCOOD-(water)$_3$ complex, and (d) HCOOD-(water)$_4$ complex.

Fig. 5(a), the most energetically favored approach for the first H_2O to formic acid is via the formation of O–H---O and C=O---H hydrogen bond. Comparing Figs. 5(a) and 5(b), we found the C–H band frequency being blueshifted 33 cm^{-1} as the second water molecule is connected to the formic acid-water complex via the weak C–H---O interaction. This finding is consistent with the contraction of the C–H bond length in the C–H hydrogen-bonding formic acid dimers.[7] Applying high pressure seems to further shorten the C–H bond, as the trend of blueshift in frequency was revealed in Figs. 3 and 4, respectively. Nevertheless, prominent redshift of about 5 and 27 cm^{-1} is predicted in the cyclic structures in Figs. 5(c) and 5(d), respectively. Both hydrogen-bond cooperative and geometric effects are attributed to the redshift in C–H frequency in the cyclic isomeric structures in Figs. 5(c) and 5(d). As in Fig. 5(c), where the two water molecules function both as proton donor and proton acceptor in the cyclic linkage, the C–H bond is weakened due to the concerted coupling. The hydrogen-bond cooperativity is greatly enhanced as the fourth water molecule is connected in Fig. 5(d), corresponding to a prominent redshift to the frequency of 2969 cm^{-1}. Thus, hydrogen-bonding nonadditivity and the size of water clusters are suggested to be responsible to cause the redshift in C–H stretching mode upon dilution of HCOOD with D_2O as indicated in Fig. 1(a).

Figure 6 shows the optimized structure of $(HCOOD)_2$-$(D_2O)_n$ complexes. As the cluster increases in size, the number of low-lying isomers exponentially increases, while only the contributions lowest in energy are reported in Fig. 6. The predicted bonded C–H stretching frequencies are 2979, 3007, 2989, 2971, and 2957 cm^{-1}, corresponding to Figs. 6(a)–6(e), respectively. A blueshift in frequency is predicted via the weak C–H---O interaction comparing Figs. 6(a) and 6(b) while the redshift in frequency was also revealed as the concentration of D_2O increases in Figs. 6(b)–6(e).

IV. CONCLUSION

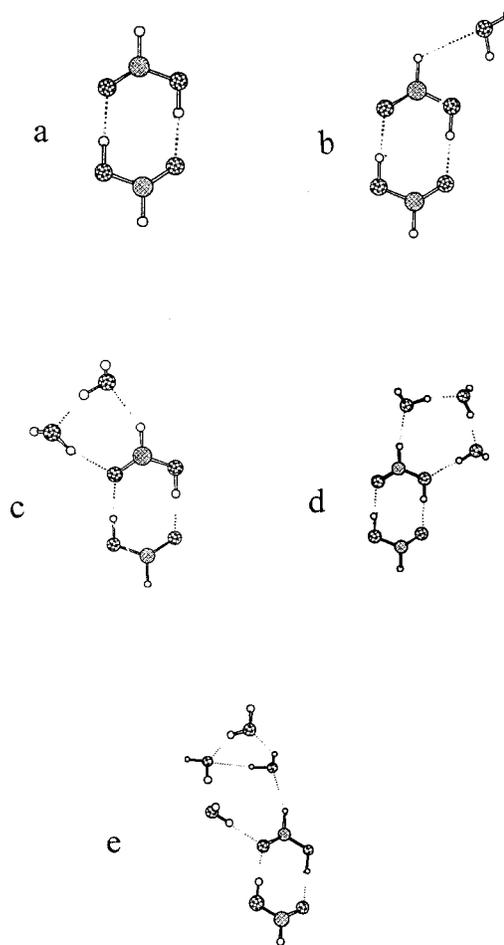In this work, we demonstrate that pressure can have a pronounced effect on C–H---O interactions in HCOOD/D_2O

FIG. 6. Optimized structure of the (a) $(HCOOD)_2$ complex, (b) $(HCOOD)_2$-(D_2O) complex, (c) $(HCOOD)_2$-$(D_2O)_2$ complex, (d) $(HCOOD)_2$-$(D_2O)_3$ complex, and (e) $(HCOOD)_2$-$(D_2O)_4$ complex.

mixtures. The frequency of the C–H stretching mode, characterizing the C–H---OD_2 interactions, increases with increasing pressure. This behavior may be attributed to the strengthening of C–H---O electrostatic/dispersion interaction as the pressure is elevated. Hydrogen-bonding nonadditivity and the size of water clusters are proposed to cause the redshift in C–H stretching mode upon dilution. The experimental results are compared to *ab initio* calculations with models of monomer and cyclic dimer of formic acid.

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