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学 位 論 文 題 目 Studies on intermolecular interaction of acetic  
acid: hydrogen-bonding and charge-transfer interaction  
in neat liquid, aqueous solutions, and gas phase  
clusters with benzene cations

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## 論文内容の要旨

Intermolecular interaction is a principal subject of chemistry for understanding the nature of substances and chemical reactions. For example, hydrogen-bonding interactions in such as O-H $\cdots$ O, N-H $\cdots$ O and N-H $\cdots$ N pairs are very important as well as hydrophobic interaction in structural biology. In recent years, other types of intermolecular interactions are recognized to play important roles in biological macromolecules. It is found that not only the typical hydrogen bonds that involve electronegative nitrogen and oxygen atoms but also the C-H $\cdots$ O hydrogen bond must be considered in the determination of protein structures. In addition to the C-H $\cdots$ O hydrogen bond, intermolecular interaction between a positively charged ion and an electron rich organic molecule (cation- $\pi$  interaction) is frequently seen on the protein surfaces which is exposed to aqueous solvation effecting on the protein structures. Charge transfer is an essential factor in an accurate description of the cation- $\pi$  interaction. These studies suggest that quantitative understanding of the charge transfer interactions between fundamental molecules of biological importance is indispensable particularly for the study of protein structures and functions.

Carboxyl group is a common functional group in living bodies. It is contained in numbers of biologically important molecules; therefore a deep understanding of many biological phenomena should be based on the knowledge of the intermolecular interaction of carboxylic groups with each other or with other molecules. It is known that molecules with carboxylic groups show specific hydrogen-bonding interactions with each other or with other hydrogen-donating or -accepting molecules. Intermolecular interaction of acetic acid has long been studied as a prototype system of carboxylic compounds. Because acetic acid has four hydrogen-donor sites (a hydroxyl hydrogen and three methyl hydrogens) and two acceptor sites (a hydroxyl oxygen and a carbonyl oxygen) in a molecule, various kinds of hydrogen-bondings can be expected in various situations. In addition to the hydrogen bond formation, non-bonding orbitals of acetic acid can interact with virtual orbitals of positive charged ions as electron-donors.

In order to understand the nature of intermolecular interaction of carboxyl group, the present study is devoted to investigating the structures of liquid acetic acid, acetic acid aqueous solutions, and acetic acid-

benzene cation complexes.

In chapter II, liquid structure of acetic acid is studied experimentally and theoretically. Experimentally, Raman spectra of acetic acid at various temperatures between 287 and 348 K are measured in the region of 15–3700  $\text{cm}^{-1}$ . Theoretically, ab initio molecular orbital calculations are performed on the Raman activities of seven cluster species of acetic acid molecules. The Raman spectrum (in  $R(\bar{\nu})$  representation) of crystalline acetic acid at 287 K shows six distinct bands in the 15–300  $\text{cm}^{-1}$  region. These bands broaden on the melting of the crystal, while their peak positions remain almost unchanged on the melting. These spectral changes are reproduced in the case that the liquid spectrum mainly arises from a variety of sizes of chain clusters as the fragments of the crystalline networks. The C=O stretching band becomes broadened toward higher wavenumbers and exhibits an asymmetric shape with increasing temperature. The wavenumbers calculated for the C=O stretching vibrations suggest that the strongly hydrogen-bonded C=O groups of the chain clusters show the prominent C=O band and its asymmetric shape is due to the presence of weakly hydrogen-bonded C=O groups of the same cluster species. The spectral analyses in both the low-wavenumber and the C=O stretching regions suggest that liquid acetic acid is mainly composed of the chain clusters, not the cyclic dimer. Assignments of the low-frequency Raman bands observed in the vapor and crystalline states are discussed on the basis of the calculated wavenumbers.

In chapter III, liquid structures of acetic acid aqueous solutions are studied using Raman spectroscopy and ab initio molecular orbital calculation. With the addition of water into liquid acetic acid, the C=O stretching vibration band of acetic acid shows high frequency shift from 1665  $\text{cm}^{-1}$  to 1715  $\text{cm}^{-1}$ . This means that the hydrogen-bond of the C=O group of acetic acid is not so strong as those seen in liquid acetic acid or in  $\text{CCl}_4$  solution (in which the band appears at 1668  $\text{cm}^{-1}$ ). A bent type hydrogen-bond is accountable for this observation. On the other hand, the increase of acetic acid in water drastically decreases the intensity of the hydrogen-bonded O-H stretching Raman band of water at 3200  $\text{cm}^{-1}$ . This suggests that acetic acid breaks the hydrogen-bond networks of water. Low frequency  $R(\bar{\nu})$  spectra of acetic acid/water binary solutions are reexamined with new experimental data and ab initio molecular orbital analysis of intermolecular vibrational modes. The  $R(\bar{\nu})$  spectrum of the aqueous mixture at  $x_A = 0.5$  bears a very close resemblance to that of the

acetic acid/methanol mixture with  $x_A = 0.5$ , indicating that the molecular complexes responsible for the Raman spectra are acetic acid clusters. The calculated low-frequency Raman feature of a side-on type dimer with bent-type hydrogen-bonds based on ab initio molecular orbital theory reproduces the observed Raman pattern nicely. Any evidence of the formation of stable acid-water pairs is not found in the low frequency Raman spectra. Furthermore, an isosbestic point is seen in the region of  $0.1 \leq x_A$  (mole fraction of acetic acid)  $\leq 0.5$ , and another one is also observed in  $0.5 \leq x_A \leq 1.0$ . The observed spectra in the region of  $0 < x_A < 0.5$  are reproduced simply by linear combinations of the pure water spectrum and the spectrum at  $x_A = 0.5$ . These results strongly suggest the presence of the two microphases with homogeneously associated molecules: a water cluster phase and an acetic acid cluster phase. The spectral change in  $0.5 < x_A < 1.0$  is attributed to the coexistence of the acetic acid cluster phase in aqueous environment and the acid associated phase characteristic of liquid acetic acid.

The author demonstrates geometrical and electronic structures of acetic acid-benzene cation complex,  $(\text{CH}_3\text{COOH}) \cdot (\text{C}_6\text{H}_6)^+$ , experimentally and theoretically in chapter IV. Experimentally, a vibrational spectrum of  $(\text{CH}_3\text{COOH}) \cdot (\text{C}_6\text{H}_6)^+$  in the supersonic jet is measured in the 3000-3680  $\text{cm}^{-1}$  region using an ion-trap photodissociation spectrometer. An electronic spectrum is also observed with this spectrometer in the 12000-29600  $\text{cm}^{-1}$  region. Theoretically, ab initio molecular orbital calculations are performed for geometry optimization and evaluation of vibrational frequencies and electronic transition energies. The vibrational spectrum shows two distinct bands in the O-H stretching vibrational region. The frequency of the strong band (3577  $\text{cm}^{-1}$ ) is close to that of the O-H stretching vibration of acetic acid (3583  $\text{cm}^{-1}$ ) and the weak one is located at 3617  $\text{cm}^{-1}$ . On the basis of geometry optimizations and frequency calculations, the strong band is assigned to the O-H stretching vibration of the *cis*-isomer of acetic acid in the hydrogen-bonded complex (horizontal *cis*-isomer). The weak one is assigned to the vertical *trans*-isomer where the *trans*-isomer of acetic acid interacts with the  $\pi$ -electron system of the benzene cation. The weakness of the high frequency band in the photodissociation spectrum is attributed to the binding energy larger than the photon energy injected. Only hot vertical *trans*-isomers can be dissociated by the IR excitation. The electronic spectrum exhibits two bands with intensity maxima at 17500  $\text{cm}^{-1}$  and 24500  $\text{cm}^{-1}$ . The calculations of electronic

excitation energies and oscillator strengths suggest that charge transfer bands of the vertical *trans*-isomer can be observed in this region in addition to a local excitation band of the horizontal *cis*-isomer. The 17500 cm<sup>-1</sup> band is attributed to the charge transfer transition of the vertical *trans*-isomer and the 24500 cm<sup>-1</sup> band is assigned to the  $\pi$ - $\pi$  transition of the horizontal *cis*-isomer. The calculations also suggest that the charge transfer is induced through the intermolecular C $\cdots$ O=C bond formed between a carbon atom of benzene and the carbonyl oxygen atom of acetic acid.

In chapter V, geometrical structures of acetic acid monomer-benzene dimer cation cluster, (CH<sub>3</sub>COOH)·(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub><sup>+</sup>, and acetic acid dimer-benzene dimer cation cluster, (CH<sub>3</sub>COOH)<sub>2</sub>·(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub><sup>+</sup>, are investigated. A vibrational spectrum of (CH<sub>3</sub>COOH)·(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub><sup>+</sup> in the supersonic jet is measured in the 2800-3700 cm<sup>-1</sup> region using the ion-trap photodissociation spectrometer. An electronic spectrum of this cluster cation is also observed with this spectrometer and a time-of-flight type spectrometer in the 6000-24500 cm<sup>-1</sup> region. For (CH<sub>3</sub>COOH)<sub>2</sub>·(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub><sup>+</sup>, vibrational and electronic spectra are observed in the regions of 2740-3700 cm<sup>-1</sup> and 6000-27000 cm<sup>-1</sup>, respectively. In order to clarify the assignment of vibrational bands, vibrational spectra of the deuterated cluster cations, (CD<sub>3</sub>COOD)·(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub><sup>+</sup> and (CD<sub>3</sub>COOD)<sub>2</sub>·(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub><sup>+</sup>, are measured. The electronic spectrum of (CH<sub>3</sub>COOH)·(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub><sup>+</sup> show a broad and strong band in the near-IR region and another band at 22750 cm<sup>-1</sup>. This spectral feature resembles that of benzene dimer cation, (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub><sup>+</sup> which has a strong charge resonance (CR) band in the near-IR region and a local excitation (LE) band with an absorption cross section one order smaller than the CR band. This fact suggests that the ion core of (CH<sub>3</sub>COOH)·(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub><sup>+</sup> is (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub><sup>+</sup>. In the vibrational spectrum of (CH<sub>3</sub>COOH)·(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub><sup>+</sup>, a strong band is located at 3084 cm<sup>-1</sup> and two weak bands are observed at 3585 and 3627 cm<sup>-1</sup>. From comparison between the vibrational spectra of (CH<sub>3</sub>COOH)·(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub><sup>+</sup> and (CD<sub>3</sub>COOD)·(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub><sup>+</sup>, the strong band is assigned to the C-H stretching vibration of (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub><sup>+</sup>. As mentioned above, the frequency of the free O-H stretching vibration of acetic acid monomer in the gas phase is 3583 cm<sup>-1</sup>. Thus, the band at 3585 cm<sup>-1</sup> is assigned to the free O-H stretching vibration of the *cis*-isomer of acetic acid in (CH<sub>3</sub>COOH)·(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub><sup>+</sup>. The band at 3627 cm<sup>-1</sup> is attributed to the O-H stretching vibration of the *trans*-isomer of acetic acid, because its frequency is predicted to be 51 cm<sup>-1</sup> (without scaling) higher than that of the *cis*-isomer at the CASSCF(4,3)/6-31G(d,p) level. In the electronic spectrum

of  $(\text{CH}_3\text{COOH})_2 \cdot (\text{C}_6\text{H}_6)_2^+$ , CR and LE bands are also observed. Therefore, the ion core of  $(\text{CH}_3\text{COOH})_2 \cdot (\text{C}_6\text{H}_6)_2^+$  is  $(\text{C}_6\text{H}_6)_2^+$ . The vibrational spectrum of  $(\text{CH}_3\text{COOH})_2 \cdot (\text{C}_6\text{H}_6)_2^+$  show very broad band from 3400  $\text{cm}^{-1}$  to 2740  $\text{cm}^{-1}$  with several peaks and no band is observed in the free O–H stretching vibrational region. On the basis of the vibrational spectrum of  $(\text{CD}_3\text{COOD})_2 \cdot (\text{C}_6\text{H}_6)_2^+$  measured in the present study and the reported IR spectrum of the cyclic dimer of acetic acid in argon matrix, the vibrational spectrum of  $(\text{CH}_3\text{COOH})_2 \cdot (\text{C}_6\text{H}_6)_2^+$  is regarded as a superposition of those of  $(\text{C}_6\text{H}_6)_2^+$  and the acetic acid cyclic dimer. This indicates that  $(\text{C}_6\text{H}_6)_2^+$  weakly interacts with the cyclic dimer of acetic acid in  $(\text{CH}_3\text{COOH})_2 \cdot (\text{C}_6\text{H}_6)_2^+$ .

## 論文の審査結果の要旨

本論文は、酢酸分子を中心とし、酢酸純液体、結晶、水溶液中の酢酸、気相中での酢酸とベンゼン陽イオン、および、酢酸とベンゼン二量体陽イオンにおける会合構造を取り扱っており、これまでの一般的常識とされていた酢酸の会合構造に関する知識を大きく修正する内容を含んでいると共に、酢酸分子を電子供与体とするこれまでには未知であった新しい電荷移動相互作用を報告している。

媒体の相互作用を受けない気相では、酢酸分子は環状の2量体を形成する。この2量体構造は、安定化エネルギーが2量体の中でも群を抜いて大きいと、液体のような凝縮相においても安定な構造体として存在すると言われてきた。しかし、酢酸結晶では、分子が2次元の鎖状会合構造をとっており、会合に伴って大きな双極子モーメントを発生し、鎖間の双極子-双極子相互作用によって更なる大きな安定化が起こっている。申請者は、低振動数ラマン分光法によって酢酸結晶が融解する過程を詳細に検討し、その分子間振動スペクトルは、融解に伴ってクラスター生成に起因する  $50\text{cm}^{-1}$  以下の信号の著しい増加と線幅の増大を示すものの、バンドの中心周波数は基本的には変化しないことから、液体酢酸は結晶が持つ鎖状構造が分断されて生じた鎖状クラスターの集合体となっていることを示唆した。更に、これらモデルクラスターの分子軌道法計算から求めた安定化エネルギーのサイズ依存性から、観測された分子間振動スペクトルの構造が鎖状クラスター構造モデルによって再現されること、また、この大きな鎖状クラスターが環状会合体集合よりもエネルギー的に有利になりうることを示した。同様の手法を、水-酢酸混合系に適用し、濃度変化に伴い分子間振動スペクトルに2種の等強度点が現れることを発見し、この系には、酢酸分子同士の鎖状クラスター状態、酢酸分子2個が最も大きな双極子モーメントを生じるサイド-オン型会合体をユニットとするクラスター状態、そして水同士が選択的に会合している水クラスター状態が系の中でマイクロな相分離状態として出現していることを示した。

一方、カルボキシル基に孤立電子対を持ち電子に富む酢酸分子と、電子が不足しているベンゼンカチオンあるいはベンゼン2量体カチオンとの相互作用を、分子線サイズ選別イオントラップ光解離分光法によって調べた。電子スペクトルには、1:1会合体では2種の分子間電荷移動バンドが観測されたが、ベンゼン2量体カチオンとの錯体ではこのような電荷移動バンドは観測されず2量体カチオンの電荷共鳴バンドが強く観測された。赤外振動スペクトルとの対応、及び、多種の励起配置構造を取り入れた分子軌道計算から、電荷移動吸収帯を与えるのは、ベンゼン環の垂直方向から酢酸分子のカルボニル基が配位した錯合体であり、逆に、1:2会合体では酢酸はベンゼンの水平面からその水素原子に水素結合的に付加していることを明らかにした。

以上の研究内容は4報の国際誌論文として既発表ないし印刷中となっており、その独創性も十分に高いことから、提出論文は審査に合格したものと判定した。

小杉健太郎君の博士論文に関する口述試験は1月25日に実施された。酢酸の低振動数 Raman 分光及び酢酸・ベンゼンカチオン2量体の分子線サイズ選別イオントラップ光解離分光法による研究を中心に約2時間半に亘って、博士論文の発表とその内容および基礎となる事柄についての活発な質疑応答がなされた。特に酢酸・ベンゼンカチオン2量体については構造に関して詳細にいたるまで質疑応答が行なわれた。この結果、同君の研究内容は独創的な展開を含み、多くの重要な新知見を与えるものであると認められた。

語学力については、博士論文が明晰な英語で書かれており、既発表の英文論文等からも十分な

水準に達していると判断された。更に、1月29日の公開発表会では、時間の関係で博士論文の一部についての簡潔な報告がなされ、質疑応答が行われた。この結果、審査員全員一致して合格とした。