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学 位 論 文 題 目　　Theoretical studies of water clusters containing

　　　　　　　　　　　OH{e}HO structure and electron-hydrogen bond

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論文内容の要旨

Water cluster anions $(H_2O)_n^-$ are the model systems for the hydrated electron. Experimentally, small cluster anions with $n = 2, 3, ...,$ have been found in the mass spectra and these photoelectron spectra have been observed. Recently, the infrared spectra for $n = 5, 6, ...,$ have also been reported. He has studied small water cluster anions $(H_2O)_n^-$ for $n = 2, 3, 4$ and 6 with ab initio MO methods. It has been believed that for small cluster anions, the excess electron is bound by the dipole moment of the neutral cluster and is distributed outside of the cluster. This type of cluster anions are the dipole bound electron type anions. On the other hand, for larger clusters with $n > 32$ or so, it has been shown that by the quantum simulation calculations that the excess electron is trapped inside the cluster. This type of cluster anions are the internally trapped electron type anions. In the $(H_2O)_n^-$, especially for the dipole bound electron type anions, the excess electron has a diffuse nature, and therefore he uses diffuse function sets to describe the excess electron in the calculations. Because the optimized geometries of the $(H_2O)_n^-$ are sensitive to the electron correlation, it is necessary to include the electron correlation at least MP2 level in the geometry optimization process. He found that there exist the internally trapped electron type isomers for small cluster anions as well as the dipole bound electron type isomers. For the dipole bound electron type isomers, the singly occupied molecular orbital (SOMO) is very diffuse and the effect of the excess electron on the structure of the core cluster is small. Consequently, the optimized structures for the dipole bound electron type isomers are close to those of the neutral clusters. For the internally trapped electron type isomers, the electron plays an important role to hold the stable structure. In the internally trapped electron anions he obtained for dimer, trimer, tetramer and one of hexamer anions, there is no hydrogen bond between the fragments surrounding the electron. For the internally trapped electron type anions, he calls the structure of the electron and the surrounding OH bonds OH{e}HO structure. For $(H_2O)_n^-$, he found that the SOMO extent measure (SEM), which is the volume of the sphere containing a half of the SOMO electron and a measure of the extent of the SOMO electron distribution, have a clear correlation with the vertical detachment energy (VDE). When SEM become large, VDE become decreasing. For tetramer and hexamer anions, he also calculates the harmonic vibrational spectra. It is shown that the shifts $|\Delta\nu_{OH}|$, which are the deviations from the average of two OH modes of free water molecule, of the OH bond interacting with the excess electron, which he calls {e}HO bond, in the double proton acceptor water molecules are larger than those of the other {e}HO bonds and $|\Delta\nu_{OH}|$ of hydrogen bonded OH bonds can be larger than those of {e}HO bonds. For hexamer anions, he has shown that the isomer which have two double proton acceptor water molecules and four membered ring structure also have qualitatively similar infrared spectrum with the experimental one.

The water cluster complexes containing a group 1 metal $M(H_2O)_n$ are another model system for the hydrated electron. The observed ionization threshold energies (ITEs) of $M(H_2O)_n$ (M = Li, Na and Cs) show several interesting features. Their ITEs are converged at $n = 4$ and their limiting values are independent of the metal element contained in the cluster. He has studied $M(H_2O)_n$ (M = Li and Na), for $n = 3, 4, 5$ and 6 with ab initio MO methods. The optimized geometries and the vertical ionization energies (VIEs) of several isomers for each M and n are obtained at MP2 level of approximation. To characterize the SOMO of the obtained isomers, he has introduced three measures; SEM, R({e}–M) and R({e}–H). R({e}–M) is the distance between the center of the electron ($R_{\{e\}}$) and the metal atom. R({e}–H) is a distance between $R_{\{e\}}$ and the hydrogen atoms. The obtained isomers can be classified into three types (surface, quasi-valence and semi-internal) by SEM and R({e}–M). In the surface type isomers, the electron is distributed on the surface of the cluster. In the quasi-valence isomers, the metal atom is not fully ionized and the SOMO is similar to a diffuse sp^n hybrid orbital of the metal atom. The isomers of the semi-internal type has an ion pair structure, $M^+(H_2O)_m \cdot (H_2O)_{n-m-j} \cdot (H_2O)_j$. In the water cluster anion part $(H_2O)_j$, there is the OH{e}HO structure. He can interpret the anormalities of the experimental results assuming that the observed isomers are semi-internal type isomers. For the semi-internal type isomers, the VIEs are mainly determined by the local structure of the anion part, $(H_2O)_j$, and the electrostatic potential from the hydrated metal cation part, $M^+(H_2O)_m$. The potential (V_{SOMO}) on the SOMO electron could be written as $V_{SOMO} = V_{SOMO}^{HMI} + V_{SOMO}^{WC}$, where V_{SOMO}^{HMI} is a long range potential of the $M^+(H_2O)_m$ and V_{SOMO}^{WC} is a short range potential of $(H_2O)_j$. He found that V_{SOMO}^{HMI} is almost independent of M and also found that the isomers which have $M^+(H_2O)_4$ as the hydrated metal cation part are the isomers with lowest VIE. When the cluster becomes large, V_{SOMO}^{HMI} and V_{SOMO}^{WC} change oppositely and cancel each other which results in the constant VIE for $n > 4$. In the $M(H_2O)_n$, OH{e}HO structure has important role to determine the VIE. He has calculated the harmonic vibrational spectra of $M(H_2O)_n$ for M = Li and Na, $n = 3, 4, 5$ and 6. In the calculated spectra for the surface type isomers, it is typical that there are the bands which have large intensities and these bands corresponds OH vibrational modes of {e}HO bonds. For quasi-valence type isomers, the frequency shifts $|\Delta v_{OH}|$ of {e}HO modes are small. For semi-internal type isomers, the shifts $|\Delta v_{OH}|$ of {e}HO modes can be large and comparable to those of hydrogen bonded HO modes. The correlation of the shifts $|\Delta v_{OH}|$ with the OH bond lengths R(O–H) for the {e}HO bonds is almost same to that of the hydrogen-bonded OH bonds. The plot of $|\Delta v_{OH}|$ against the R(X···H) (X = O for hydrogen bond and X = {e} for the interaction between the electron and OH bonds in the OH{e}HO structure), shows that there are two series for {e}HO bonds and $|\Delta v_{OH}|$ for {e}HO can be as large as -550 cm^{-1} which is close to the maximum $|\Delta v_{OH}|$ for the hydrogen-bonded OH bond. The data on these two series corresponds to different

schemes to interact with the electron. The $|\Delta \nu_{OH}|$ can be treated as a measure of the strength of the interaction between the electron {e} and the OH bonds. There are several features which are similar to those of hydrogen-bonded OH bonds. He calls the interaction between the electron and the surrounding OH bonds the electron-hydrogen bond. The {e}OH bond in the double proton-acceptor water molecules are as strong as hydrogen bonds. The frequency shifts of {e}HO bonds in the double proton-acceptor water molecules are as large as -550 cm^{-1}.

論文の審査結果の要旨

　　本論文は、水の負イオンクラスターおよびリチウム、ナトリウムの水和クラスターの構造、垂直電子脱離エネルギー、OH 伸縮基準振動数などを、十分な広がりをもつ基底関数系を用いて電子相関を考慮した分子軌道法によって計算を行い、OH{e}HO 或は {e}HO という電子-水素原子水素結合によってこれらが安定化しているという新しい概念を提出している。

　　まず、$(H_2O)_n^-$ （n=2,3,4,6）について構造、赤外吸収振動スペクトル、垂直電子脱離エネルギー（VDE）等の計算を行った。実験結果から、これらのクラスターは中性クラスターの双極子によって電子が結合していると言われていた。実際、計算ではこのような双極子結合電子型のクラスターの存在も確かめられたが、新しい「電子内部束縛型の負イオンクラスター」の存在が見出された。このクラスターでは、電子を取り囲む水分子の間には直接の水素結合は存在せず、それぞれの水分子の水素原子が電子と強く結合することによって安定化するという、これまでに考えられなかった構造をとっている。また、一電子被占軌道（SOMO）にある電子の 1/2 が占める体積空間を SOMO Extent Measure（SEM）と定義し、これが VDE と明瞭な相関があることを示した。SEM が大きいほど電子の脱離が起こりやすくなり VDE は減少する。また、{e}HO 結合に伴って観測される、O-H 伸縮振動数の変化と O-H 間の距離との相関が、通常の水素結合とまったく同じ線上に乗ることから、{e}HO 結合は本質的には通常の水素結合と同じ性質をもっていることを証明し、{e}HO 結合の概念を確立した。

　　リチウムやナトリウムなどの 1 族金属の水和錯体、$M(H_2O)_n$ についてもその構造とイオン化エネルギーの計算を行った。実験的には、n=4 でイオン化閾エネルギー（ITE）はある値に収束するが、その値は金属原子の種類に無関係でありバルクの水の ITE に等しいことが知られている。この系の特徴を記述するために、SEM の他に、金属あるいは水素原子と SOMO 電子の中心座標間の距離、それぞれ R({e}-M) および R({e}-H) の評価を行った。これらの値の違いにより、得られたクラスターの構造は、表面型、擬似原子価型、半内部型に分類された。表面型では SOMO 電子がクラスターの表面に分布しており、擬似原子価型では金属が完全にイオン化しておらず、SOMO 電子は金属の広がった sp^n 混成軌道に類似している。また、半内部型のクラスターでは、イオン対構造、$\{M^+(H_2O)_m\}(H_2O)_{n-m-1}(H_2O)_1^-$ をとっているのが大きな特徴である。このイオン対のなかの負イオン部分 $(H_2O)_1^-$ は、OH{e}HO 構造をとっており、実験的に観測されたクラスターの構造が半内部型をとっていると仮定すると実験結果を説明することができる。また、このような半内部型クラスターの VDE はクラスターの負イオン部分の局所構造によって決まってくることを示した。更に、n=4 でイオン化閾エネルギーが一定値を取るのは、長距離ポテンシャルと近距離ポテンシャルがお互いに相殺し合うためであることを見出した。

　　以上のように、鶴澤君は水分子の水和負イオンクラスターおよびアルカリ金属水和クラスターの構造研究に新しい概念を提出し、分子クラスター研究に大きな貢献を果たしたと言えるであろう。これらの結果は 4 報の国際誌に報告されており、審査委員全員一致して審査に合格したものと判定した。