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## 論文内容の要旨

In the present work, spectroscopic splittings due to the proton tunneling, so-called 'tunneling splittings', in the ground states of cations have been studied for tropolone (TRN), 9-hydroxyphenalenone (9-HPO-h) and its deuterated compound (9-HPO-d). These molecules have intramolecular hydrogen bonds and are spectroscopically well-known in the neutral ground state ( $S_0$ ) as well as in the lowest singlet excited state ( $S_1$ )<sup>1,2</sup>. However, no spectroscopic study has so far been published concerning the cation ground state ( $D_0$ ).

The main purpose of this study is to clarify a relative importance of the geometrical and electronic factors of molecules in determining the rate of proton tunneling. The molecules TRN, 9-HPO-h and 9-HPO-d have O-H-O (or O-D-O) chelate moieties. The geometrical factor is the length of traveling proton which is basically attributable to a ring planality of the carbon skeletal ring. For example, in TRN, the increase of the ring planality causes two oxygen atoms to approach each other. This effect accelerates the proton tunneling. On the other hand, the electronic factor is the charge distribution of each atom. These molecules are known to have aromaticity. The change in aromaticity caused by ionization also plays a crucial role in changing the rate of proton tunneling. In this way, the proton tunneling behavior in the cation  $D_0$  state depends on the balance between the structural and electronic factors. It should be very interesting to investigate this situation spectroscopically.

The present thesis is mainly concerned with the photoelectron spectroscopic study with high-resolution threshold photoelectron spectroscopy (2 cm<sup>-1</sup> resolution) combined with a resonantly enhanced

multiphoton ionization (REMPI) technique. The advantage of this method is to be able to select individual  $S_1$  tunneling doublet components as resonant intermediate states. Only photoelectron vibrational peaks corresponding to transitions terminating on levels with the same symmetry should appear. The tunneling splitting width in the cation  $D_0$  state may be obtained by comparing the total transition energy (excitation and ionization energies).

First, in the case of the TRN molecule, the transition energy shift between the two transitions originating from the both tunneling doublet components in the neutral  $S_0$  state has not been observed within the present experimental accuracy ( $2\text{cm}^{-1}$ ). This energy shift reflects the difference in the doublet separation between the  $S_0$  and  $D_0$  states. Taking into account of the reported splitting width in the  $S_0$  state ( $0.3\text{cm}^{-1}$ , by Redington et al<sup>1</sup>), it can be concluded that the zeroth vibrational level in the cation  $D_0$  state is nearly degenerate; namely, the proton tunneling is inhibited. On the basis of other photoelectron spectra obtained by exciting other vibronic bands in the  $S_1$  state, vibrational assignments were carried out with the aid of the  $\Delta v=0$  propensity rule. However, no tunneling splitting was observed in any vibrational mode. Reported molecular orbital calculations of TRN show a relatively rich  $\pi$ -electron population of the ketonic oxygen. This theoretical result supports a classical viewpoint of large contribution from polar structure which promotes proton tunneling. In the cation  $D_0$  state accessed by  $\pi$ -electron removal, there seems to be less contribution from the polar structure. This tendency is thought to prevent the intramolecular hydrogen bond from forming.

The second molecule studied in the thesis is 9-HPO-d. In the case of this molecule, a transition energy shift of  $11\text{cm}^{-1}$  has been observed between the two transitions originating from individual tunneling doublet components in the  $S_0$  state. From an splitting width of  $12\text{cm}^{-1}$  in the ground state reported by Bondybey et al.<sup>2</sup>, the splitting width in the cation

$D_0$  state can be calculated to be  $1\text{cm}^{-1}$ , which within the experimental error limit of the present work. The 9-HPO-d molecule has a molecular structure consisting of three condensed benzene skeletons with two aromatic rings. It is expected that the large molecular skeletal deformation affecting the distance between the two oxygen atoms does not occur upon photoionization. In such a rigid molecule, the electronic factor is more important than the geometric factor for explaining the inhibition of proton tunneling in the cation  $D_0$  state, compared with the neutral  $S_0$  state.

Summarizing these results, from the high-resolution REMPI threshold photoelectron spectroscopy, it has been found that the proton tunneling of both TRN and 9-HPO-d molecules is inhibited in the cation  $D_0$  state. As far as the geometrical and electronic factors are concerned, the inhibition of proton tunneling in the cation  $D_0$  state has been explained in terms of a reduction of charge density on the ketonic oxygen. This effect is thought to be the main reason for weakening the intramolecular hydrogen bonds in these two molecules. Finally, the accurate adiabatic ionization potentials have been determined for the first time as follows;

$$I_a(\text{TRN}) = 68365 \pm 5\text{cm}^{-1}.$$

$$I_a(9\text{-HPO-h}) = 65338 \pm 5\text{cm}^{-1}.$$

$$I_a(9\text{-HPO-d}) = 65350 \pm 5\text{cm}^{-1}.$$

## References

1. R. L. Redington et al., J. Chem. Phys. 88, 627 (1988).
2. V. E. Bondybey et al., J. Chem. Phys. 80, 5432 (1984).

## 論文の審査結果の要旨

尾関博之君の学位論文は、高分解能の共鳴多光子イオン化－しきい光電子分光法を用いて、分子内水素結合を持つ分子の陽イオン基底状態におけるトンネル効果について研究したものである。とり上げた分子はトロポロンおよび9-ヒドロキシフェナレノンで、共に分子内水素結合の存在が知られ、中性分子の基底状態及び励起状態においてトンネル効果による振動準位の分裂が観測されている。これらの分子がカチオンになったときのトンネル効果の様子を調べるという目的をもって、同君は所属する研究室で開発された高分解能の光電子分光法を利用して測定を行った。実験装置、手法の重要な部分は既存のものを用いているが、それらを着実に自分のものにしており、結果の解析も慎重に行われている。測定の結果は、両分子とも測定精度 ( $\sim 1 \text{ cm}^{-1}$ ) の範囲内でトンネル効果による分裂は観測されなかった。カチオンについてトンネル効果の影響が少ないことに対し、本論文では電子状態的な要因と構造的な要因の双方から見た詳しい考察を行っている。現状では定性的な考察にとどまっているが、その内容は合理的なものであると判断される。以上、実験・解析がきちんと行われていること、及び従来例のなかったカチオンの分子内水素結合の様子を調べることに成功したこと等を総合して、本論文は学位授与の対象として十分なものであると判定する。