Observation of Intramolecular Hydrogen Bonds of *o*-Fluorophenol Ions by Using Autoionization Detected Infrared Spectroscopy

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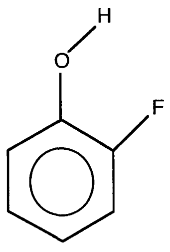
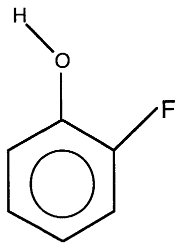
Intramolecular hydrogen-bonded OH stretching vibration for o-fluorophenol ion is observed by using a newly developed technique for infrared spectroscopy of isolated molecular ions.

In the last decade, various multi-laser spectroscopic techniques have been developed to observe vibrational transitions of ultracold isolated molecules, as well as clusters in supersonic jets.[1] Very recently we proposed a new infrared (IR) spectroscopic technique for jet-cooled molecular ions.[2] In this technique, we observe vibrational transitions of very high Rydberg states instead of the bare ion. Because of extremely weak interaction between the ion core and Rydberg electron, the ion core of the high Rydberg states is regarded as the same as the bare ion. This similarity has been widely confirmed in extensive studies of zero kinetic energy photoelectron spectroscopy (ZEKE-PES).[3] Since the IR absorption of the Rydberg states is followed by autoionization and the yield spectrum of the resultant ions is observed, we call this new technique "autoionization detected infrared spectroscopy (ADIRS)".

In this letter, we apply ADIRS to observe the OH stretching vibration for o-fluorophenol ion. The o-fluorophenol molecule is one of the prototypes of intramolecular hydrogen-bonded systems. There are two isomers with respect to the conformation of the hydroxyl group as shown below.



cis



trans

Only the cis isomer has an intramolecular hydrogen bond between the F atom and the hydroxyl group. Figure 1 shows the multiphoton ionization spectrum at the origin region for S_1-S_0 transition of ultracold o-fluorophenol in a molecular beam. In the previous dispersed fluorescence study, band (A) was assigned to be the 0-0 band of the cis isomer, and band (B) was to that of the trans isomer.[4] Recently infrared-ultraviolet double resonance spectroscopy was applied to these two "isomers", presenting the OH stretching vibrations in their neutral ground states.[5] The result, however, revealed that both bands must be associated with one of the isomers, because both have the same OH stretching frequency. Therefore, it was concluded that the previous assignment was wrong, and both the bands have been re-assigned for the cis isomer.

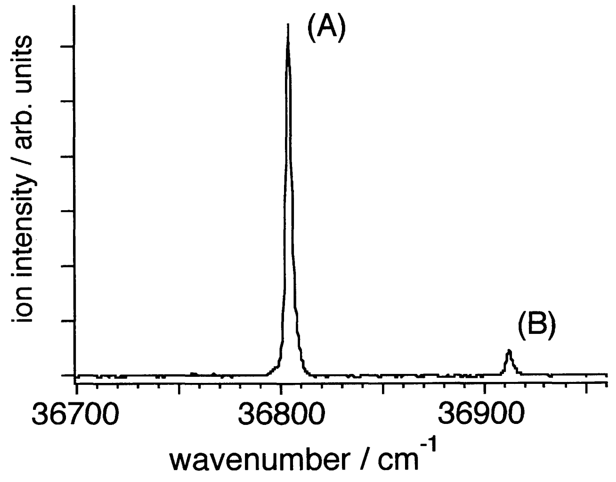


Figure 1. Multiphoton ionization spectrum of o-fluorophenol for the band origin region of the S_1-S_0 transition.

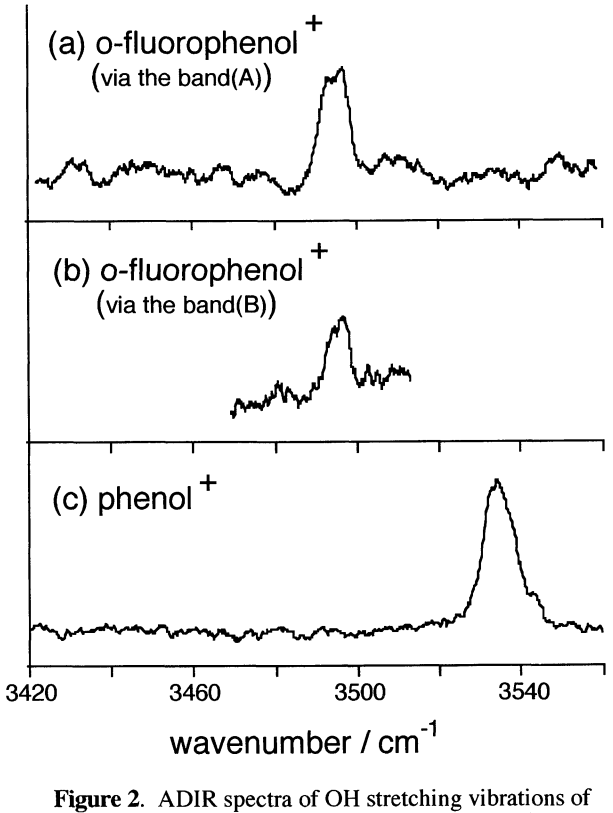


Figure 2. ADIR spectra of OH stretching vibrations of (a), (b) o-fluorophenol cation, and (c) phenol cation, respectively. The spectrum (c) is reproduced from ref.2.

Figure 2 shows the OH stretching region of ADIR spectra of the ultracold (a), (b) o-fluorophenol ion, and (c) the phenol ion, respectively. For the spectra (a) and (b), o-fluorophenol was first excited to the S_1 state by the ultraviolet (UV) laser tuned at the bands (A) and (B) shown in Figure 1, respectively. Secondly, another UV laser pumped the molecule to very high Rydberg states lying about 10 cm^{-1} below the first ionization threshold (principle quantum number ≈ 100). Finally, the tunable infrared laser light was introduced to excite the ion core of the Rydberg states. The vibrationally excited ion core decays through autoionization, leading to the ejection of the Rydberg electron. By monitoring the resultant ions, infrared absorption can be sensitively detected. The IR spectra were obtained by scanning the infrared laser wavelength as ion yield spectra.

The sample was seeded in He gas of 3 atm stagnation pressure, and was expanded into vacuum through a pulsed nozzle. The molecular beam was formed by using a skimmer, and was introduced to an interaction region. Produced ions were extracted by a pulsed electric field, which was applied after a delaytime of 100 ns from the photoexcitation, and mass-selected by a time-of-flight mass spectrometer.

It has been well known that hydrogen-bond formation leads to substantial red-shifts of OH stretching vibrational frequencies in both neutral and ionic states.[6] Both the OH stretching frequencies of the o-fluorophenol ion show clear red-shifts from that of the phenol ion, indicating presence of an intramolecular hydrogen bond in the former. To our knowledge, this is the first observation of the intramolecular hydrogen-bonded OH stretch in the *isolated molecular ion.*

Table 1. The OH stretching vibrational frequencies of phenol and o-fluorophenol (cis isomer) in cm^{-1}

	phenol	*o-fluoro-phenol*	*red-shift from phenol*
neutral	3657[a]	3634[b]	23
cation	3534[c]	3495[d]	39

[a]Ref.1. [b]Ref.5. [c]Ref.2. [d]This work.

In addition, the spectra (a) and (b) in Figure 2 clearly show that both the OH stretch bands appear at the same position. This indicates that both bands are associated with the same isomer, that is the cis isomer in which an intramolecular hydrogen bond is expected. This is consistent with the IR spectroscopic result for the neutral ground state.[5]

The vibrational frequencies of the OH stretch for (cis) o-fluorophenol in the neutral and cationic ground states are listed in Table 1 together with phenol. The red-shift is more significant for the cation. This means that the intramolecular hydrogen bond becomes stronger in the cation. The same tendency has been generally observed for intermolecular hydrogen bonds. It has been shown that the extent of the red-shift of OH stretching vibrations is a good indicator of hydrogen bond strength. In case of phenol containing hydrogen-bonded clusters, a few hundreds cm^{-1} red-shifts of vibrational frequencies are typically observed even for neutral clusters.[7] The small red-shift indicates that the intramolecular bond of o-fluorophenol is very weak both in the neutral and ionic states.

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References and Notes

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