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LETTERS

Autoionization-Detected Infrared Spectroscopy of Molecular Ions

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A new method for infrared spectroscopy of cold molecular ions is proposed, and its application to the phenol ion is presented. Very high Rydberg states converging to the first ionization threshold are prepared by two-color double-resonance excitation. Vibrational excitation of the ion core of the Rydberg states induces autoionization, leading to the molecular ion. An infrared spectrum is obtained by monitoring the ion current as a function of the vibrational excitation laser frequency. The observed spectrum practically provides the vibrational frequency of the bare ion.

Introduction

For highly excited Rydberg states, it is well-known that the geometric structure of their ion core is quite similar to that of the corresponding bare ion, because of a very small interaction between the ion core and a Rydberg electron. Zero kinetic energy-photoelectron spectroscopy (ZEKE-PES)[1] and mass-analyzed threshold ionization (MATI) spectroscopy[2] have been developed on the basis of this nature of high Rydberg states to provide precise vibrational frequencies of ionic species. Both techniques have been widely applied as vibrational spectroscopy of various molecular and cluster ions; however, there is a difficulty in obtaining high-frequency vibrations, such as OH and CH stretches. This difficulty comes partly from poor Franck−Condon factors between the ground and Rydberg states and also from band congestion in electronic transitions used as the final step of the measurement.

Weak interaction between the ion core and a high Rydberg electron enables us to perform “isolated-core excitation”, in which only the ion core is subject to photoabsorption and the Rydberg electron behaves as a spectator during the transition. In the isolated-core excitation, thus, transitions of the ion core are practically regarded as same as those of the corresponding bare ion. This phenomenon was first applied for generation of doubly excited atoms.[3] Johnson and co-workers measured electronic transitions of benzene and phenol ions by detecting the electronic autoionization signal following the isolated-core excitation of high Rydberg states.[4−6] They called this method photoinduced Rydberg ionization spectroscopy (PRIS).

In this Letter, we apply the isolated-core excitation for vibrational spectroscopy of molecular ions. Very high Rydberg states with the cold ion core are prepared by two-color double-resonance techniques. Vibrational excitation of the ion core results in vibrational autoionization (autoionization accompanied by vibrational de-excitation),[7] and ion signal is monitored as a function of the frequency of tunable infrared light. Infrared spectroscopy has an advantage in the observation of high-frequency vibrational modes, so that this method provides us with complementary information to ZEKE-PES and PRIS. We observe the OH stretching vibration of the phenol ion as an application of this new infrared spectroscopy.

Experiment

Figure 1 shows the excitation scheme of the method. Jet-cooled neutral phenol is excited to very high Rydberg states converging to the vibrationless level ($v = 0$) of the ground state of the ion by using two-color double-resonance excitation via the 0−0 band of the S_1-S_0 transition. The infrared (IR) laser light excites the isolated ion core of the Rydberg states to the

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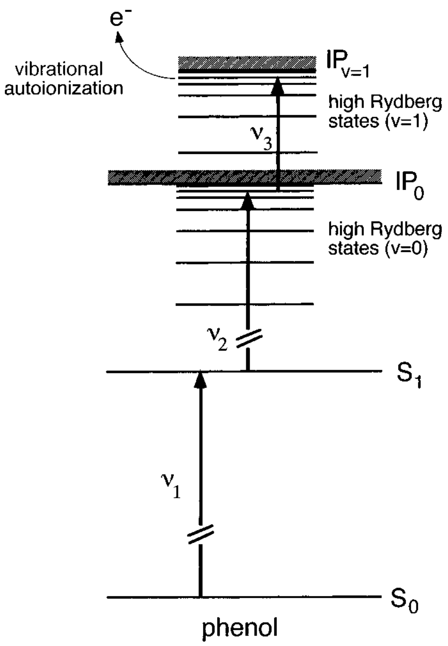

Figure 1. Excitation scheme of autoionization-detected infrared spectroscopy of the phenol ion. ν_1 and ν_2 are ultraviolet laser light to pump the molecules to high Rydberg states. ν_3 is infrared light to excite a vibration of the ion core of the Rydberg states.

vibrational excited level ($v = 1$). Because of the vibrational energy of the ion core, the core-excited Rydberg states lie above the first ionization threshold. Energy exchange between the ion core and a Rydberg electron results in the spontaneous ejection of the electron, i.e., vibrational autoionization. After an appropriate delay time, a pulsed electric field is applied to the interaction region, and the ions produced by autoionization are extracted into a time-of-flight mass spectrometer. The ions are mass-analyzed and detected by an ion detector. Monitoring the autoionization signal, the infrared wavelength is scanned.

Two ultraviolet (UV) beams were used to excite phenol to high Rydberg states. One was the second harmonic of the output of a dye laser with C540A dye pumped by a pulsed YAG laser. Its typical output power was a few tens of nanojoules per pulse and was kept low enough to avoid generating one-color ion background signal. The other UV beam was the second harmonics of the output with DCM dye, and its typical power was about 0.5 mJ. Both laser beams were introduced coaxially into a vacuum chamber after they passed through a lens of $f = 500$ mm. The IR light was prepared by difference frequency generation between the second harmonics of a YAG laser and an output of a YAG pumped dye laser. The output power of the IR light was typically 1 mJ/pulse and was focused by a lens of $f = 250$ mm. The IR beam was counterpropagated with the UV laser beams. Pulse widths of all the laser beams were 5 ns. No delay time was provided between the UV pulses, while the IR light was introduced 5 ns after the UV excitation.

A time-of-flight mass spectrometer of the Wiley-McLaren type[8] with a 60 cm long flight tube was used. The pulsed electric fields were 25 and 125 V/cm for ion repelling and for extraction, respectively. The pulse duration was 8 μs, and the pulse rising rate was 15 V/ns. We discuss the field ionization effect of the Rydberg states[9] later.

Phenol vapor was seeded in He gas of 3 atm stagnation pressure and was expanded into the vacuum chamber through a pulsed valve. The typical background pressure of the chamber was 7×10^{-6} Torr. Jet expansion was skimmed by a skimmer of 2 mm diameter, and the resulting molecular beam was introduced into the interaction region.

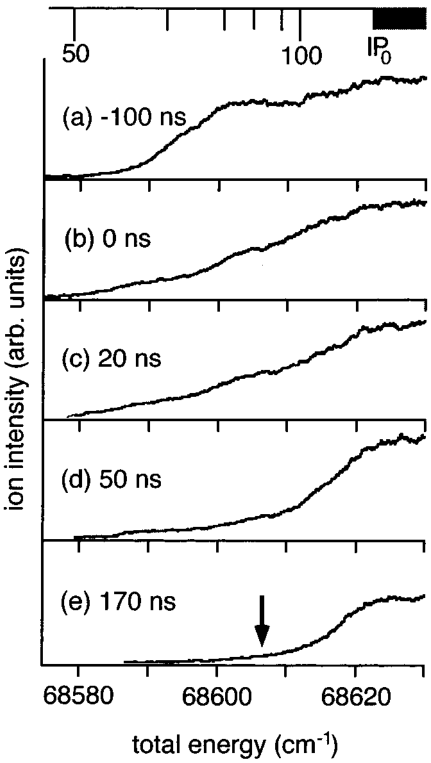

Figure 2. Two-color multiphoton ionization spectra of phenol. In the spectra, the ν_1 wavelength is fixed to the 0−0 band of the S_1−S_0 transition of phenol (36 348 cm^{-1}) and the ν_2 wavelength is scanned. The delay time between the laser excitation and rise of the pulse electric field is changed from (a) −100 ns to (e) 170 ns. Approximate principal quantum numbers of the Rydberg states are shown on the top of the spectra. The arrow indicates the wavelength of the excitation lasers for the measurement of the infrared spectrum shown in Figure 3.

Results and Discussion

Figure 2 shows two-color multiphoton ionization spectra of phenol near the first ionization threshold (IP$_0$). The first excitation laser was fixed to the 0−0 band of the S_1−S_0 transition of phenol (36 348 cm^{-1}),[10] and the second laser wavelength was scanned. Parts a−e of Figure 2 represent the change of the threshold with respect to the delay time between the laser pulses and the rise of the pulsed electric field. Since IP$_0$ of phenol has been found at 68 623 cm^{-1},[1] the ionization signals below the threshold come from field ionization of high Rydberg states conversing to the $v = 0$ level of the ion. On the top of the figure, approximate principle quantum numbers (n) of the Rydberg states are indicated (zero quantum defects of the Rydberg states are supposed). With increase of the delay time, the field ionization signal decreases and the observed threshold shifts to IP$_0$, because the Rydberg states decay to disappear, presumably due to predissociation. From these delay time dependence, we estimated the lifetime of the high Rydberg states: about 80 ns for the $n = 80$ state.

For the IR spectroscopy, we fixed the second excitation laser wavelength at 68 607 cm^{-1} in total energy (corresponding to the $n = 83$ Rydberg state), and the delay time was set to 170 ns to avoid background ion signals due to field ionization. The infrared laser was introduced and its wavelength was scanned over the 3 μm region. Monitoring the ion signal, the infrared spectrum shown in Figure 3 was obtained; an intense peak appears at 3534 (±1) cm^{-1}. From the band position, this peak is uniquely assigned to the OH stretching vibration of the ion core.

Infrared spectra of the phenol ion in the 3 μm region have been measured by the “messenger method”, in which a rare

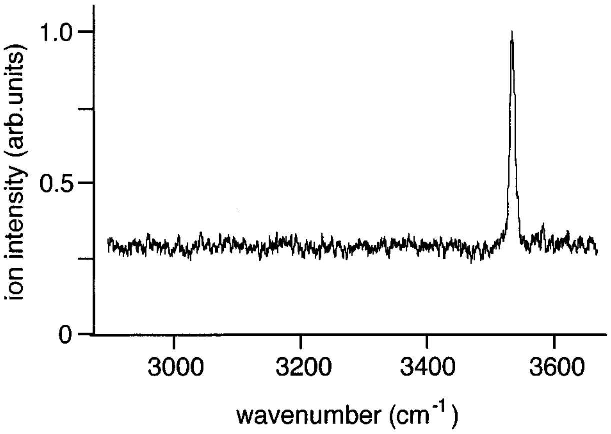

Figure 3. Autoionization-detected infrared spectrum of the phenol ion in the 3 μm region.

gas atom is attached to the bare ion and vibrational predissociation of the cluster ion is detected.[11,12] Because of the weak interaction between the rare gas atom and the molecular ion, the observed frequency is expected to be close to that of the bare ion. In fact, the messenger method gave us 3535 (±2) cm^{-1} for the OH stretch of the phenol ion. This value agrees with the present result within the experimental error. Perturbation from the Rydberg electron to the ion core is much smaller than that from rare gas atoms combined by van der Waals forces. Also the Rydberg state was prepared by two-color excitation of the jet-cooled molecule so that the rotational temperature in the present method is kept cold. Therefore, the observed frequency 3534 cm^{-1} in the present method is expected to be more reliable than that obtained by the messenger method. The accuracy is essentially as same as that in ZEKE-PES measurements of vibrations of molecular ions. Moreover, in case of the infrared spectroscopy, there is no problem of absolute frequency shifts due to the extraction field as in ZEKE-PES.

For autoionization-detected infrared spectroscopy, there are some points to be noted:

(1) The signal to noise (S/N) ratio of the observed infrared spectrum was restricted by the field ionization background. The background is greatly reduced with the long delay time (170 ns) between the Rydberg state excitation and ion extraction, since almost all of the Rydberg molecules that are not ionized by the infrared light decay before the pulsed electric field is applied. The fluctuation of the background signal, however, hides weak CH stretching vibrations expected around 3070 cm^{-1} (the infrared intensities of the CH stretches are estimated to be about $^{1}/_{10}$ of that of the OH stretch[13]). Further improvement of the S/N ratio can be achieved by using multiple electric field pulses, which separate the time-of-flight of the infrared (autoionization) induced ions from those of field ionization ions. This has been performed in MATI and PRIS studies.[2,4-6]

(2) The band intensity in this method depends not only on the infrared absorption intensity but also on the dynamics of the Rydberg states. Decay dynamics of core-excited Rydberg states is characterized by complicated competition between autoionization and neutral decay (mainly predissociation).[14] The appearance of the vibrational spectrum suggests that the neutral decay rate, which is roughly estimated as 80 ns at $n = 80$, is not faster by far than the autoionization rate.

For infrared spectroscopy of jet-cooled ionic species, dissociation spectroscopy has been popular;[15] the messenger method described above is also based on the same concept. Though the dissociation spectroscopy is appropriate for cluster ions, in which a weak intermolecular bond is included, it is hard to apply to bare molecular ions, in which much higher energy is required to break a chemical bond. In contrast, the autoionization detected infrared spectroscopy can be widely applied to bare molecular ions. Further applications to molecular ions having an intramolecular hydrogen-bond are now in progress in our laboratory.

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