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Electronic spectra of solvated NH_4 radicals $NH_4(NH_3)_n$ for $n = 1 - 6$

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Abstract. Electronic absorption spectra of $NH_4(NH_3)_n$ $(n = 1 - 6)$ were measured in the energy region of 4500–14 000 cm^{-1}. The spectra were assigned to the transition derived from a $3p^2F_2 - 3s^2A_1$ Rydberg–Rydberg transition of NH_4. A drastic decrease of excitation energy from the transition of NH_4 (15 062 cm^{-1}) down to 5800 cm^{-1} for $NH_4(NH_3)_4$ cluster was observed, while there was no clear difference for $n = 4$, 5, and 6. Successive binding energies of $NH_4(NH_3)_n$ in the $3p$-type state determined from the spectra were found to decrease monotonically with increasing n, in a similar manner to those of a positive ion, NH_4^+. The drastic spectral change was ascribed to spontaneous ionization of NH_4 in ammonia clusters.

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1 Introduction

Electron localization modes in a finite system have been one of the most important subjects in cluster research. In particular, negatively charged cluster ions of polar solvent molecules have been investigated extensively in relation to bulk solvated electrons [1]. Another interesting target has been the clusters of alkali metal atoms solvated with polar molecules. Ionization potentials of these clusters have been determined as a function of the number of solvent molecules [2, 3]. Photoelectron spectra of the negatively charged alkali-atom-solvent clusters have also been investigated [4–6]. The results indicate a drastic change in the electronic structure of alkali atoms in clusters, which suggests spontaneous ionization of metal atom in clusters.

NH_4 is a typical hypervalent Rydberg radical, and its spectroscopic properties have been studied extensively for free NH_4 [7], since the work by Herzberg [8]. This radical has also been considered to be an important intermediate in solution chemistry [9]. Possible existence of an NH_4 radical in reactions of solvated electrons and in electrochemistry has been assumed for many years. Since NH_4 is isoelectronic with an alkali atom, the solvated NH_4 clusters may serve the purpose of investigation on interaction between a Rydberg electron and surrounding polar solvent molecules. The structure and stability of ammoniated NH_4 have been investigated theoretically by Kassab *et al.* [10, 11]. In our previous works, ionization potentials of $NH_4(NH_3)_n$ have been determined by photoionization threshold measurement [12]. Formation and decay processes of NH_4 in ammonia clusters have been examined by using a femtosecond pump-prove technique [13].

In the present work, electronic absorption spectra of ammoniated NH_4 radicals were studied by a photodissociation technique coupled with a time-of-flight mass spectrometry. The electronic transition of $NH_4(NH_3)_n$ $(n = 1 - 6)$ derived from the $3p$–$3s$ Rydberg–Rydberg transition of free NH_4 were examined down to 4500 cm^{-1}. Based on these results, the mechanism of stabilization for NH_4 and localization modes of the Rydberg electron in ammonia clusters was discussed.

2 Experimental

We used a vacuum system consisting of a differentially evacuated chamber, which includes a cluster source, and a reflectron-type time-of-flight (TOF) mass spectrometer. Ammonia clusters were generated by supersonic expansion of pure ammonia from a pulsed nozzle (General valve, series 9). Ammonia (NH_3, minimum purity of 99.99%, Nippon Sanso) was used without further purification. $NH_4(NH_3)_n$ were produced through photodissociation of ammonia clusters at 193 nm by the use of an ArF excimer laser (Lamda Physik, LPX205) [12]. Photoabsorption spectra were recorded by the measurement of the depletion yield of each cluster ion through photodissociation with the pump laser (4500–14 000 cm^{-1}). We used two light sources as the pump laser; one is an idler output of an optical parametric oscillator (Spectra Physics, MOPO-730), the other is an output at the difference between a dye laser (Quanta Ray, PDL-3), and a YAG fundamental (1064 nm). After irradiation of the pump laser, the clusters remained in the molecular beam were probed by photoionization at 355 nm or at 266 nm by using the third or fourth harmonic of a YAG laser (Spectra Physics, GCR-250), respectively. Delay time between the ArF excimer laser and the pump laser was typically 100–200 ns, while that between the pump and the probe lasers was typically 10–50 ns. In order to improve a S/N ratio, we adopted a dual beam configuration as follows. The excimer laser and the probe laser were split into dual beams, and introduced colinearly and counterpropagatedly to an acceleration region of the mass spectrometer, while the pump laser beam was introduced colinearly with one of the beams. The cluster ions produced were accelerated and introduced to a field-free region of the TOF mass spectrometer. The ions were reflected by electric fields at the end of the TOF chamber and were detected by a dual microchannel plate after flying back into the field-free region. Output signals were fed into a digital storage oscilloscope (LeCroy 9242A) after being amplified by a wide-band amplifier (NF Electronic Instruments, BX-31). A typical mass spectrum is presented in Fig. 1. The photoabsorption cross section, σ, was determined to be

$$\sigma = \ln(I_{\mathrm{off}}/I_{\mathrm{on}})/\phi \qquad (1)$$

where ϕ was the photon fluence, and I_{on} and I_{off} were the signal intensities of ions in the mass spectrum with and without irradiation of the pump laser beam, respectively [14].

3 Results and discussion

The $3p$–$3s$ Rydberg–Rydberg transition of free NH_4 has been observed in the visible region and its 0–0 band is located at $15\,062\ \mathrm{cm}^{-1}$ [8]. Upon solvation, this transition may shift to the red as was found to occur in the isoelectronic complex, e.g., $Na(NH_3)_n$ [4,15]. Figure 2 shows the electronic absorption spectra of $NH_4(NH_3)_n$ ($n = 1-6$) in the energy region of 4500–14 000 cm^{-1}. As shown in the figure, the absorption band of the 1:1 complex consists of an onset at around 9300 cm^{-1} and an intense maximum at 11 700 cm^{-1}. From the comparison with the spectrum of free NH_4, we can safely assign this band to the transition derived from the $3p$–$3s$ transition of NH_4. Measurement of high-resolution spectra for the 1:1 complex is underway and will be reported elsewhere [16]. For $n = 2$, 3, and 4, the absorption bands exhibit a broad maximum at $\approx 9000\ \mathrm{cm}^{-1}$, $\approx 7000\ \mathrm{cm}^{-1}$ and $\approx 5800\ \mathrm{cm}^{-1}$, respectively, which show successive redshifting with increase of cluster size, while there are no clear differences among the bands for $n = 4$, 5, and 6.

For $NH_4^+(NH_3)_n$ ($n = 1-4$), successive binding energies have been determined by Kebarle and coworkers, and they decrease monotonically with increase of cluster size; 1.08, 0.68, 0.60, and 0.54 eV for $n = 1-4$, respectively [17]. The successive binding energies of $NH_4(NH_3)_n$ in neutral ground states have also been determined in our previous work. The numbers are much smaller than those in the ionic state: 0.34, 0.12, 0.26, and 0.30 eV for $n = 1-4$, respectively [12]. Based on these results, as well as the spectra in Fig. 2, we determined the binding energies of $NH_4(NH_3)_n$ in the $3p$-type state, on the assumption that onsets of the absorption bands correspond to the transition from the ground state to the potential minimum of the $3p$-type state. The binding energy for $n = 1$ was obtained as 0.98 eV, which was almost equivalent to that in the ionic state, and was much larger than that of the ground state. For $2 \leq n \leq 4$, the binding energies were found to be almost equivalent, ≈ 0.44 eV, and were in the middle between those of the neutral ground and the ionic states. On the other hand, the binding energy decreased suddenly between $n = 4$ and $n = 5$. For $n = 5$ and 6, the binding energies were found to be 0.24 and 0.19 eV, respectively, and were almost the same as those of the neutral ground state, which are 0.24 and 0.20 eV, for $n = 5$ and 6, respectively [12]. These results show that the first solvation shell completes with four NH_3 molecules, as in the case of $NH_4^+(NH_3)_n$ and that, for the larger clusters, further NH_3 molecules are bound to the first-shell NH_3 with weaker hydrogen bonds. These arguments are in accord with the theoretical studies by Kassab and Evleth [10,11].

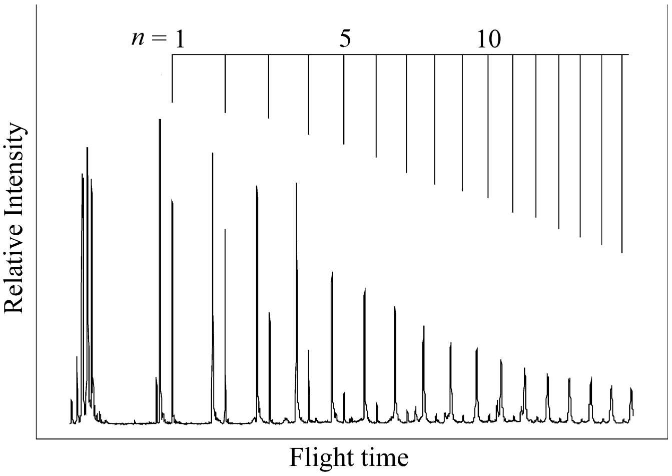

Fig. 1. Typical mass spectrum of $NH_4(NH_3)_n$ generated by an ArF excimer laser at 193 nm and ionized by a fourth harmonic of a YAG laser at 266 nm. Large peaks were generated by two-photons ionization of the excimer laser. Distance between the large and the small peaks corresponds to the time delay between the excimer laser and the fourth harmonic of the YAG laser (200 ns).

The result is that the binding energy of $NH_4{-}NH_3$ in the $3p$-type state is equivalent to that in the ionic state, indicating that interaction between NH_4 and NH_3 in the $3p$-type state is as ionic as that in the positive ion. The theoretical calculation for density distribution of the $3s$-type electron in $NH_4(NH_3)_n$ ($n \leq 6$) have predicted that the $3s$-type electron is localized on the nitrogen atom of the NH_4 for $n = 0-2$, while the electron is delocalized over the NH_3 molecules for $n = 3$ and 4 [10]. If this is the case, the electron delocalization in the $3p$-type state is expected to be more extensive, because the $3p$-type electron is more loosely bounded. Similar to the present results, rapid decrease in a ${}^2\mathrm{P} - {}^2\mathrm{S}$ energy separation of the sol-

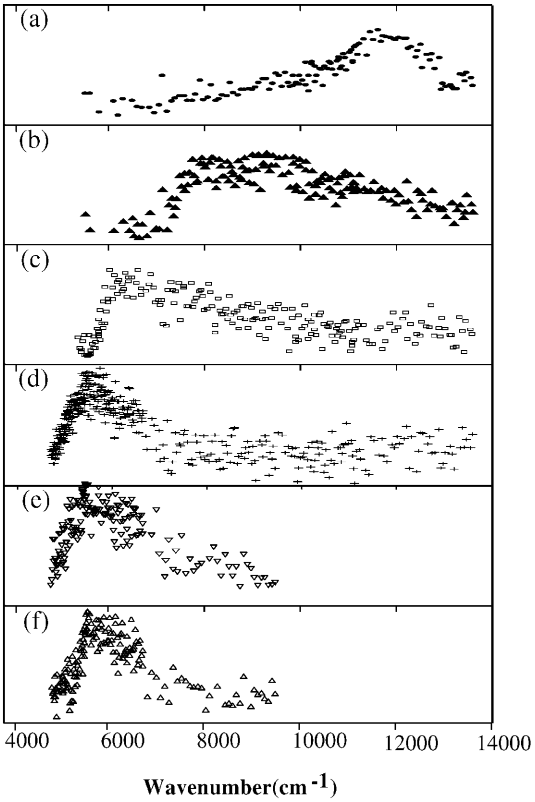

Fig. 2. Photoabsorption spectra of $NH_4(NH_3)_n$ ($n = 1-6$) in the energy region of 4500–14 000 cm^{-1}, with $n = 1$ (a) to 6 (f). These spectra were obtained by the taking into account of the yield of depletion for the cluster ions. Intensities of the spectra were normalized at their peak positions.

vated alkali atom has been observed in photoelectron spectra of $Na^-(NH_3)_n$ and $Li^-(NH_3)_n$. In the latter systems, the large spectral change has been ascribed to spontaneous ionization of metal atoms in ammonia clusters by *ab initio* calculations [4]. Therefore, these arguments suggest that the NH_4 radical is ionized in small ammonia clusters, forming a one-center ion-pair state similar to those of $Li(NH_3)_n$ and $Na(NH_3)_n$; the Rydberg electron may be squeezed out over the NH_3 molecules when the first shell is closed. In order to get further insight into the solvation state of NH_4 in these clusters, we are conducting the absorption measurements for larger $NH_4(NH_3)_n$ clusters.

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