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Electronic spectra of jet-cooled calix[4]arene and its van der Waals clusters: Encapsulation of a neutral atom in a molecular bowl

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The encapsulation of neutral guest has been studied for calix[4]arene (C4A) by forming van der Waals clusters with Ar and Ne in supersonic jets. The electronic transitions of these clusters suggest that the first Ar (Ne) is encapsulated inside the C4A cavity, while the next atoms are bound outside. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2723068]

Calixarene (CA) is known as a functional molecule exhibiting encapsulation and self-assembly.[1–3] In condensed phase, extensive NMR and x-ray diffraction studies have revealed details of the encapsulation structure and process.[4–7] In the gas phase, mass spectrometry combined with several ion source, such as electrospray, has been developed for the characterization of the encapsulation of charged guests.[8,9] For neutral guests, on the other hand, the encapsulation has been accompanied by the introduction of large substituents at *para* position. This is because the interaction energy between CA itself and neutral guests is much weaker than the case of the charged ones. To understand the intrinsic nature of the encapsulation of CA in detail, the study on the weak interaction with neutral molecules or atoms is essential, and it can be performed by the combination of supersonic jet and laser based spectroscopy.

Here, we report the first laser spectroscopic study on jet-cooled Calix[4]arene (C4A). In the present work, we focus our attention on two issues. One is the electronic state of C4A. In C4A, an exchange interaction between phenol parts removes the degeneracy of the electronic excited states and splits them into A, E, and B in C_4 point group. Among them, A and E states are dipole allowed from the ground state. In the present work, we discuss aspects of symmetric species of the electronic excited states. The other is the ability of encapsulation of weakly bound neutral guests. To answer these questions, we apply laser spectroscopy to jet-cooled C4A and its van der Waals clusters with Ar and Ne, which are the typical example of weakly bound species.

The experimental setup was described in our previous paper.[10,11] Briefly, jet-cooled C4A was generated by using a homemade heated pulsed nozzle. We measured S_1-S_0 laser-induced fluorescence (LIF), UV-UV hole burning,[12] and IR-UV double resonance spectra[13] to investigate the electronic and geometric structures of C4A and its van der Waals clusters. The observed IR spectrum was compared with a theoretically obtained one with the optimized structure at the B3LYP/6-31+G* level. C4A (98%) was purchased from Tokyo Chemical Industry Co. and the one provided from a laboratory of organic chemistry in our department. They were used without further purification.

Figure 1(a) shows the LIF spectrum of jet-cooled C4A. The lowest frequency band at 35 357 cm^{-1} is assigned to the band origin since we did not find any bands in the region lower than this band under the expansion condition with He carrier gas. As to the vibronic bands, there are seven intense bands in the 35 400–35 550 cm^{-1} region. Most of the bands appearing at 35 500–35 700 cm^{-1} are assigned to the combination bands, while no prominent progression is seen in the higher frequency region. The result indicates large anharmonicity in some of the vibrational modes and the existence of strong vibronic coupling in the S_1 state. For the assignment of the vibronic bands, measurements of dispersed fluorescence spectra may be essential, which is our future task. Besides the main vibronic feature described above, there are several vibronic bands. In order to verify the coexistence of isomers or its clusters, we measured the UV-UV hole-burning spectrum by fixing the probe laser frequency to the band origin at 35 357 cm^{-1} [Fig. 1(b)]. Comparison of the UV-UV hole-burning spectrum with the LIF spectrum suggests that almost all the peaks in the LIF spectrum are due to a single species.

The intensity pattern in the LIF spectrum provides us a good hint for the assignment of the excited states. As described above, both the A and E states are dipole allowed from the ground (A) state. However, if the transition moment of each phenol is completely perpendicular to the C_4 axis, the probability of the $A \leftarrow A$ transition becomes zero and only the $E \leftarrow A$ transition has nonzero transition probability. On the other hand, if the transition moment of each phenol is slightly tilted from a plane perpendicular to the C_4 axis, the $A \leftarrow A$ transition will have nonzero probability. In the LIF spectrum of Fig. 1(a), the intensity of the band origin is weaker than those of the three vibronic bands at ~35 530 cm^{-1}. In addition, we do not see any progression of these vibrations in the higher energy region. Thus, it is quite probable that the lowest electronic excited state is ^1A, and the strong bands around 35 530 cm^{-1} region are due to degenerate vibrations having e symmetry. These bands can appear strongly through the vibronic coupling with the E state, which is thought to be located higher than the A state.

Next, we discuss the vibrational structure of OH groups. In C4A, four OH groups are equivalent and H bonded to

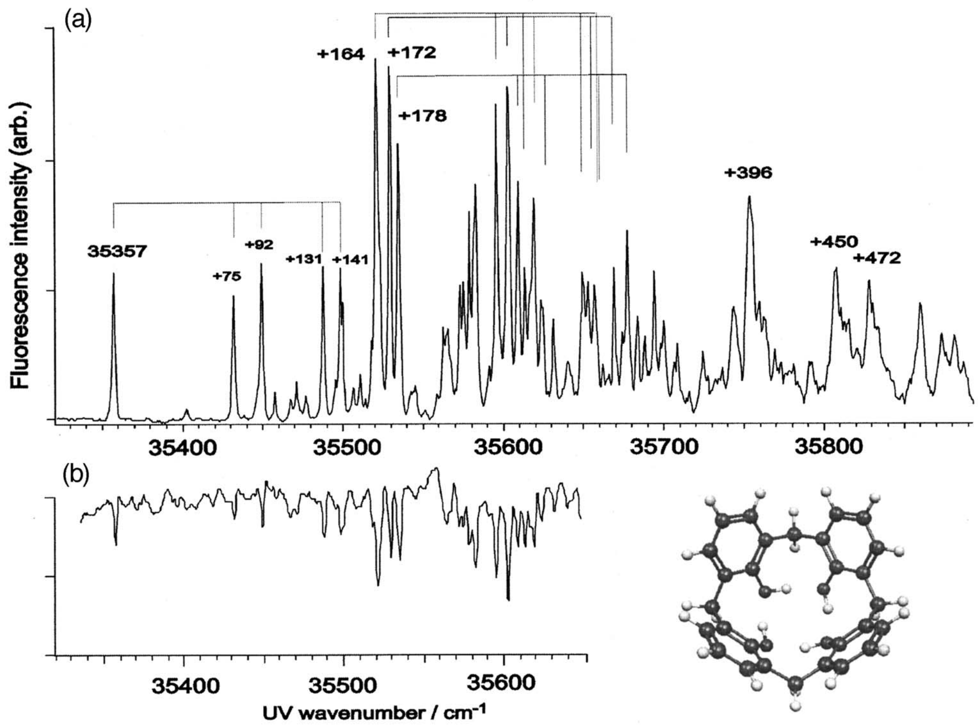

FIG. 1. (a) LIF spectrum of jet-cooled calix[4]arene. Sample was heated at 130 °C. (b) UV-UV hole-burning spectrum obtained by fixing the probe laser to the band origin at 35 357 cm^{-1}.

each other. Thus, similar to the electronic states, the OH stretching vibrations are classified into a, e, and b species in C_4 point group. Among them, the vibration(s) with e symmetry will appear strongly in the IR spectrum. The upper trace of Fig. 2 shows the fluorescence detected IR-UV double resonance spectrum obtained by monitoring the origin band. In the spectrum, an intense H-bonded OH stretch band appears at 3158 cm^{-1} and no free OH stretch band is observed. It may be helpful to compare this frequency with those of phenol dimer and trimer. In phenol dimer, the donor and acceptor OH bands are observed at 3530 and 3654 cm^{-1}, respectively.[14] In phenol trimer having a ring-form structure, the H-bonded OH stretch band appears at 3440 cm^{-1} in the IR spectrum.[14] Since the OH stretch frequency of C4A (3158 cm^{-1}) is much lower than those of phenol dimer and trimer, we conclude that the four OH groups are much more strongly H-bonded in C4A. This observation is supported by the calculated IR spectrum at B3LYP/6-31+G* level (lower trace of Fig. 2). The calculation predicts an intense degenerated OH stretch band around 3160 cm^{-1} and negligibly small IR activities for the other stretch bands.

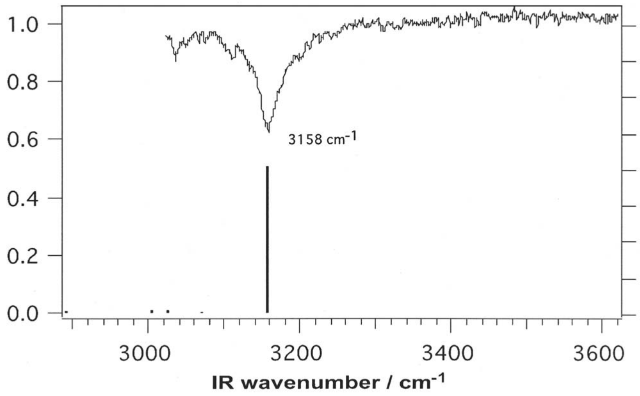

FIG. 2. (upper) IR-UV double resonance spectrum of jet-cooled calix[4]arene in the OH stretching region. (lower) Calculated IR spectrum of calix[4]arene at the B3LYP/6-31+G* level. Vibrational frequencies are scaled by a factor of 0.955.

Another important issue in this work is the investigation of the ability of encapsulation of neutral guest(s) by weak van der Waals interaction. According to the density functional theory calculation, each benzene plane is tilted by 36° with respect to the C_4 axis in C4A. Thus, a neutral guest can be captured inside the cavity by four phenol molecules. Figure 3(a) shows the LIF spectra observed at different Ar/He mixing ratios. In the figure, several new vibronic bands appear by mixing very small amount of Ar (0.09%) into He carrier gas. We found that all the new bands appearing at Ar/He=0.09% are redshifted by 45 cm^{-1} with respect to the monomer bands. These bands can be assigned to the C4A-$(Ar)_1$ cluster. The magnitude of the redshift for C4A-$(Ar)_1$ is larger than those of benzene-$(Ar)_1$ (21 cm^{-1}) (Ref. 15) and phenol-$(Ar)_1$ (34 cm^{-1}).[16]

With increasing partial pressure of Ar up to Ar/He =0.75%, the monomer bands become weaker and weaker and another new bands appear in the lower frequency region. Typical feature is seen in the band origin region and the enlarged portion is shown in Fig. 3(b). In the figure, one can see that even 0.02% Ar/He mixing ratio is enough to form C4A-$(Ar)_1$. With increasing Ar partial pressure up to Ar/He=0.6%, the origin bands of C4A-$(Ar)_{n=2-5}$ appear on the lower frequency side. Very interestingly, the magnitude of the redshift is quite different between $n=1$ and $n \geqslant 2$; that

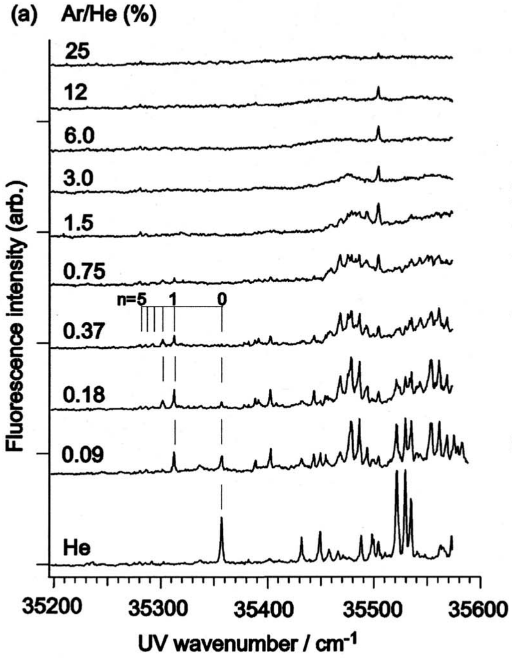

FIG. 3. (a) LIF spectra of jet-cooled calix[4]arene-$(Ar)_n$ clusters at various Ar/He mixing ratios. The total pressure was kept at 3 bars. (b) LIF spectra of jet-cooled calix[4]arene-$(Ar)_n$ clusters in the band origin region.

is, the redshift from C4A to C4A-$(Ar)_1$ is 45 cm^{-1}, while the intervals of the bands of C4A-$(Ar)_{n=2-5}$ are in the range of 11−4 cm^{-1}. Figure 4(a) shows the plot of the redshifts of C4A-$(Ar)_n$ as a function of the number of attached Ar atoms (n). The redshift due to the first atom attachment ($n=1$) is four times larger than that due to the second atom attachment ($n=2$). The shift due to further attachment seems to approach a plateau value. This result strongly suggests that the binding site of the first Ar atom is quite different from those of $n \geqslant 2$; that is, the first Ar atom is encapsulated inside of the C4A cavity, while the second, third, fourth, and fifth Ar atoms are bound outside of the cavity. Our proposed stepwise cluster formation of C4A-$(Ar)_{n=1-5}$ is shown in Fig. 4(b). We carried out a similar measurement for C4A-$(Ne)_n$, and the results are also shown in Fig. 4(a). The redshift from C4A to C4A-$(Ne)_1$ is 9.5 cm^{-1}, which is close to that predicted from the ratio of the polarizabilities of Ne (0.39 Å^3) and Ar (1.62 Å^3).[7] As seen in Fig. 4(a), the redshift due to the attachment of second Ne atom ($n=2$) is much smaller than that of the first one ($n=1$). This is the same tendency as that of C4A-$(Ar)_n$, indicating that C4A-$(Ne)_n$ has essentially the same structure with that of C4A-$(Ar)_n$. Another interesting point in Fig. 3(a) is the appearance of a sharp band around 35 517 cm^{-1} at Ar/He mixing ratios higher than 1.5%. In the spectra at Ar/He > 1.5%, most of the sharp bands disappear while the band at 35 517 cm^{-1} remains strong. The origin of this band is not clear, and further investigation is necessary

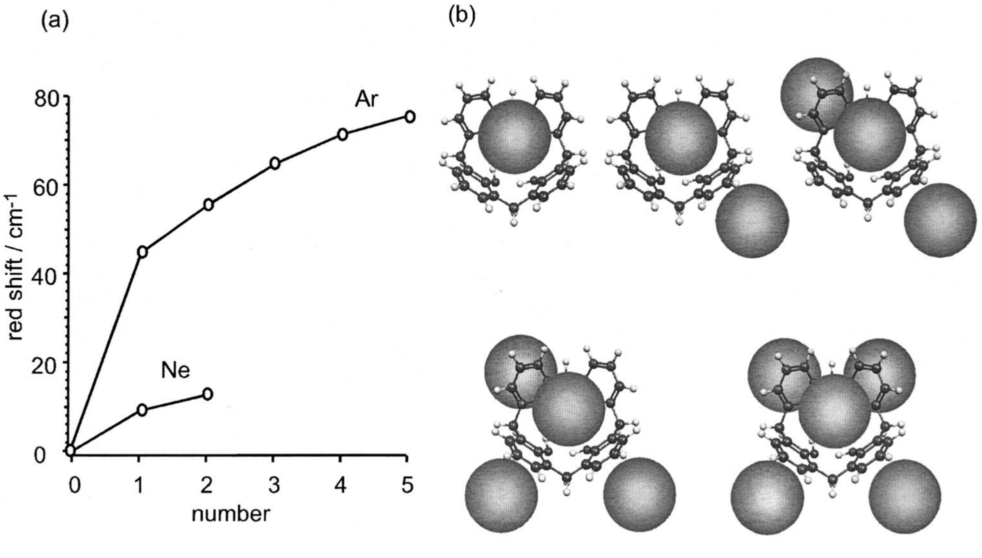

FIG. 4. (a) Plot of the redshifts of the band origin of calix[4]arene-$(Ar)_n$ and-$(Ne)_n$ as a function of n. (b) Proposed structures of calix[4]arene-$(Ar)_{n=1-5}$.

including the measurement of mass-selected multiphoton ionization spectra.

In conclusion, we present the first spectroscopic study on jet-cooled calix[4]arene and its van der Waals clusters with Ar and Ne. It was found that calix[4]arene has high ability of encapsulation of rare gas atoms and the clusters exhibit red-shifts characteristic of the binding sites. The first atom is captured inside of the calix[4]arene cavity, while the second atom is bound outside of the cavity. We would like to stress that the combination of the cooling technique by supersonic jet and sensitive laser spectroscopic method enables us to investigate the encapsulation of such a weakly bound neutral guest. The encapsulation of a variety of neutral molecules, such as water, acetonitrile, and chloroform, is in progress.

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