

Title	ゼロエネルギー電子分光法による芳香族ファンデルワールス錯体の研究
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Zero-Kinetic-Energy Electron Study of Several Aromatic van-der-Waals Complexes

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Backgrounds Molecular photoelectron spectroscopy in the gas phase provides direct information about the ionic states produced immediately upon ionization transition. A series of vertical or adiabatic ionization energies (I_a) for any molecule can be obtained by photoelectron spectroscopy, subsequently providing basic information about the energy levels of molecular cations as well as the electronic structure of the neutral molecules. Development of molecular photoelectron spectroscopy enabled spectroscopy with higher energy resolution not only in electronic excited states but also in cationic ground states.

On the other hand, molecular van-der-Waals (vdW) complexes produced in supersonic jets have attracted much interest in molecular spectroscopy for many years, because of their low binding energies, large intermolecular equilibrium distances, and very low frequency vdW vibrations. The spectroscopic study of vdW complexes in supersonic jets has been greatly advanced by the use of laser spectroscopy not only in excited states by means of LIF spectra, REMPI excitation spectra, and but also in cationic ground states by means of zero-kinetic-energy (ZEKE) electron spectra.

One of the important advantages in the laser photoelectron spectroscopy of resonantly enhanced multiphoton ionization (REMPI) with a pulsed UV laser is that cation spectroscopy can be carried out by means of a photoelectron spectroscopic technique based on state-selected photoionization for various neutral molecular species.¹ This technique is especially efficient for studying very weakly bounded vdW complexes formed in supersonic jets, since a specific vdW species can be selected out from a mixture of various analogous species, as was earlier demonstrated for the vdW complex of No with Ar.²

A two-color ZEKE electron technique has an excellent state-selectivity as well as a high-resolution spectroscopic ability of measuring rotational structure of a molecular cation.

Purposes Several aromatic vdW complexes produced with Ar and N₂ in supersonic jets have been studied by means of ZEKE electron spectroscopy based on two-color (1+1) REMPI with two kinds of tunable nanosecond UV lasers. From a spectroscopic point of view, vdW complexes are interesting because of their energy shift due to the complex formation and low-frequency intermolecular vdW vibrational modes. Also it is interesting to compare the shift of vdW vibrational frequencies, which can be observed in REMPI excitation spectra in lowest singlet electronic excited state (S_1) and in ZEKE electron spectra in cationic ground state (D_0). With the ZEKE electron spectroscopy, the precise adiabatic ionization potentials (I_a) can also be determined, and from the I_a values of bare molecule and its vdW complexes, the relations between the

dissociation energies in S_0 and D_0 can be deduced.

Results

From the ZEKE electron spectra of fluoro- benzene (FB^+) and the vdW complexes (FB-Ar^+) and (FB-Ar_2^+) *via* their S_1 0^0 bands (not shown in this abstract), their I_a values are determined as 74238, 74011, 73816 cm^{-1} , respectively. In the ZEKE electron spectra for FB-Ar and FB-Ar_2 , vdW vibrational modes have been observed on the cation origin bands. To confirm the vibrational mode appeared for FB-Ar , ZEKE electron spectra *via* S_1 vdW vibrational modes has been measured. Figure 1 shows the ZEKE electron spectra of (FB-Ar^+) vdW complex obtained *via* (a) S_1 0^0 , (b) S_1 b_y^2 , (c) S_1 b_x^2 , and (d) S_1 s_z^1 . The vdW vibration with same vibrational progressions are observed in (a), (b) and (d) in Figure 1, though the pattern of the vibrational progression has changed in (c) in Figure 1.

Discussions

In (FB-Ar^+) with C_s symmetry, there are three possible vdW vibrations; totally symmetric bending b_x^+ , non-totally symmetric bending b_y^+ , and stretching s_z^+ . Spectra (b) and (d) in Figure 1, obtained *via* S_1 b_y^2 and S_1 s_z^1 , respectively, are similar in vibrational progression to spectrum (a), consisting of four peaks with the same spacing (12 cm^{-1}), but shifted 31 and 50 cm^{-1} from the (FB-Ar^+) origin peak, respectively. These frequencies may be attributed to the vdW vibrations (b_y^{+2} and s_z^{+1} , respectively) of (FB-Ar^+), since there are a total of three vdW vibrations (b_y , b_x , and s_z). Therefore it may be concluded that the vibrational progressions in spectra (b) and (d) are due to $b_x^{+n} b_y^{+2}$ and $b_x^{+n} s_z^{+1}$, respectively, as indicated in Figure 1. On the other hand, spectrum (c) in Figure 1, which was obtained *via* S_1 b_x^2 , shows a somewhat complicated structure with almost the

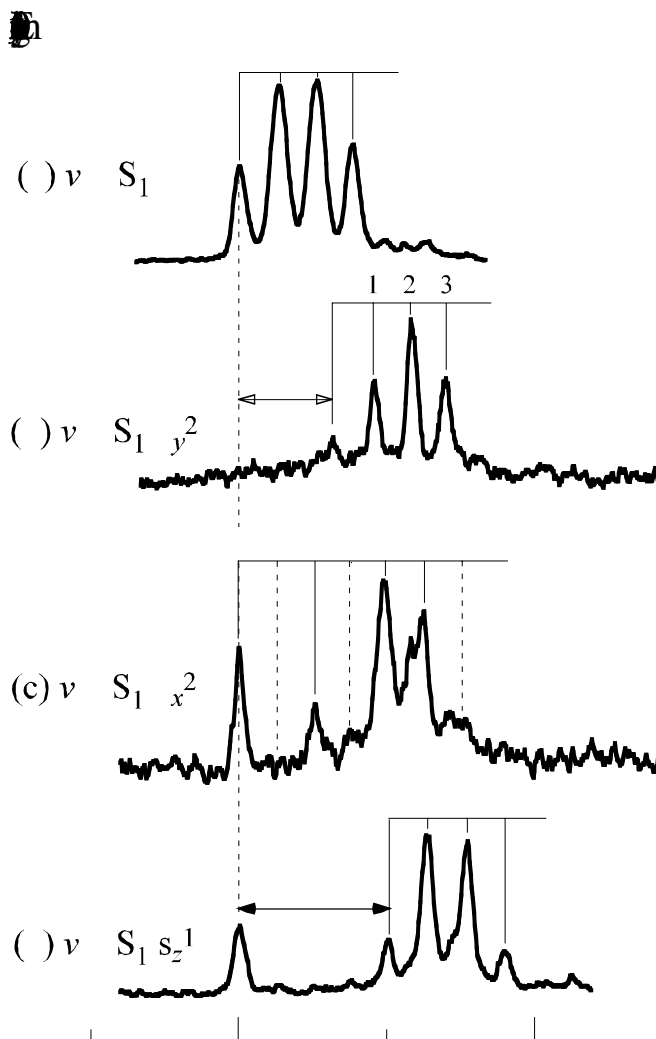


Figure 1. ZEKE electron spectra of FB-Ar vdW complex *via* S_1 vibrational levels: (a) S_1 0^0 , (b) S_1 b_y^2 , (c) S_1 b_x^2 , and (d) S_1 s_z^1 . All of the three possible intermolecular vdW vibrations have been observed.

same spacings (12 cm^{-1}) as in spectrum (a). In other words, spectrum (c) seems to be interpreted again in terms of b_x^{+n} . This has been confirmed also from my Franck-Condon calculations. Spectra (a) and (d) in Figure 1 are similar in spectral pattern to those of the corresponding MATI spectra reported by Lembach and Brutschy³ or by Grebner and Neusser⁴. However spectra (b) and (c) in Figure 1 have been obtained for the first time.

In order to confirm the assignments of the observed 12 cm^{-1} progressions observed for FB-Ar, Franck-Condon calculations were carried out for the spectra (a) and (c) in Figure 1. In each case, the same harmonic potential curve except for the potential displacement D_{bx} was assumed for the lower S_1 and the upper D_0 state. In these calculations I used an analytical expression for the overlap derived by Smith⁵. The displacement (D_{bx} for FB-Ar) between lower and the upper curve were taken as adjustable parameters. From this calculation, the displacement was deduced to be $D_{bx} = 1.45$ for FB-Ar.

In this study, all the three possible vdW vibrations have been observed experimentally in the cationic state for $(\text{FB-Ar})^+$, and they have been successfully assigned.

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