Ultraviolet laser ionization studies of 1-fluoronaphthalene clusters and density functional theory calculations

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This paper studies supersonic jet-cooled 1-fluoronaphthalene (1FN) clusters by ultraviolet (UV) laser ionization at 281 nm in a time-of-flight mass spectrometer. The $(1FN)_n^+$ (n=1–3) series cluster ions are observed where the signal intensity decreases with increasing cluster size. The effects of sample inlet pressures and ionization laser fluxes to mass spectral distribution are measured. Using density functional theory calculations, it obtains a planar geometric structure of 1FN dimer which is combined through two hydrogen bonds. The mass spectra indicate that the intensity of 1FN trimer is much weaker than that of 1FN dimer and this feature is attributed to the fact that the dimer may form the first "shell" in geometric structure while the larger clusters are generated based on this fundamental unit.

Keywords: 1-fluoronaphthalene clusters, ultraviolet laser ionization, mass spectrum, density functional theory calculation

PACC: 3640B, 8280M

1. Introduction

Molecular clusters combined via hydrogen bonding or van der Waals force are the ideal medium for investigating the science of biology, organic material and environmental science in molecular level.[1,2] Interest in the structural and dynamical properties of polycyclic aromatic hydrocarbon clusters or van der Waals complexes continues to motivate a large number of experimental and theoretical investigations.[3,4] For naphthalene and its substituents, studies are mainly focused on naphthalene dimer and naphthalene with rare gas complexes.[5−7] Das *et al.*[8] studied the electronic spectroscopy of naphthalene–acenaphthene van der Waals dimer by measuring the laser-induced fluorescence excitation, dispersed fluorescence, and two-colour hole-burning spectrum. Also quantum chemistry calculations are performed at MP2/6-31G and MP2/6-311G(d) level to predict the equilibrium structure and binding energy of the dimer. Tsuzuki *et al.*[9] calculated the intermolecular interaction energies of naphthalene dimers by using an aromatic intermolecular interaction model, and found the dispersion interaction to be the major source of attraction in the naphthalene dimer. Chakarova *et al.*[10] used a density functional (DF) which included van der Waals interactions for planar systems to calculate binding distance and energy of naphthalene dimer which are 0.41 nm and 172 meV, respectively.

Very few experimental and theoretical studies of 1-fluoronaphthalene (1FN) clusters or van der Waals complexes have been reported. Champagne *et al.*[11] studied the low and high resolution S_1–S_0 fluorescence excitation spectra of Ar–1FN and CH_4–1FN van der Waals complexes, and the CH_4–1FN complexes exhibit original bands such that each splits into three distinct subbands while such splittings are not observed in the Ar–1FN complexes. We carried out a study of 1FN dimer by one-colour resonant two-photon ionization (R2PI) spectrum in the wavelength range of 304 nm to 322 nm. The peak which at about 315 nm with a relatively broad band was assigned as the first electronic excited transition of 1FN dimer,[12] and it had the more red-shifted comparison with the original band of 1FN monomer at 313.8 nm.

In this contribution, we report the results of our studies of supersonic jet-cooled 1FN clusters by ultraviolet (UV) laser ionization mass spectrum. The purpose of our effort is to understand the cluster generation and ionization distribution and to discuss the ef-

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fects of sample inlet pressures and laser fluxes. Meanwhile, the density functional theory (DFT) calculations are performed to predict the probable structure and the binding energy of 1FN dimer.

2. Experimental

The experiments were performed with a time-of-flight mass spectrometer (TOFMS) which has been described previously.[13] The 1FN (Aldrich, 99% purity, USA) was used without further purification. The samples were heated to about 110 °C to acquire sufficient vapour, seeded into 2–3 bar of helium and expanded into the vacuum through a high temperature pulsed valve with a 0.8-mm diameter orifice. A YAG laser (Quanta-Ray Lab-150) pumped dye laser (Sirah PRSC-G-18) where the DCM dye was employed. The output of the dye laser was doubled by a KDP/SHG crystal. The final UV laser output was guided into the TOFMS chamber with an $f = 50$-cm spherical lens, intersecting the cluster beam at about 50-mm downstream from the nozzle orifice. The cluster ions were extracted by a high-voltage pulse, and then detected by a microchannel plate and averaged with a multichannel scaler (Stanford Research Systems, SR430). All the timing sequence was controlled by a digital delay/pulse generator (Stanford Research Systems, DG 535).

3. Results and discussion

3.1. Mass spectrum of 1FN cluster ions

Supersonic molecular beam is an effective route to produce molecular clusters which are stable and are combined by much weaker intermolecular forces such as dispersion forces, multipolar induction forces and hydrogen bonding.[14] There are three main factors which govern the cluster content and size distribution: the stagnation pressure, the temperature and the nozzle aperture cross section. However, higher supersonic Mach number is necessary to cool the sample enough, so lighter carrying gas, helium, higher backing pressure are chosen to assure that there are many collisions during the expansion phase. It is also hard to determine such parameters precisely. In experimental practice, such information can be indirectly monitored by simply detecting the vacuum pressure in the ionization chamber. Besides the molecular cluster generation, another important aspect is the cluster ionization process. The ionization of molecular clusters proceeds via the ionization of a single molecule in the cluster, a process which is generally accompanied with molecular excitation:

$$(\mathrm{Mol})_N \rightarrow [(\mathrm{Mol})_N^+]* \equiv (\mathrm{Mol})_{N-1}(\mathrm{Mol}^+)^* + \mathrm{e}^-. \quad (1)$$

Relaxation of the initially generated ion is usually accompanied by substantial intramolecular and intermolecular configurational changes which include cluster fragmentation and dissociative ionization. However, when large aromatic molecule embedded in a solvent cluster, where the solvent may be a rare gas, the ionization of clusters is accompanied with relatively small intra- and intermolecular configurational relaxation because of the delocalization of the positive charge in the aromatic molecule. The 1FN molecule has two aromatic rings, and the delocalization effects occurred in aromatic molecule may also happen in 1FN clusters.

The first resonant electronic transition $S_1 \leftarrow S_0$ of 1FN was studied by UV absorption spectrum[15] and fluorescence excitation spectrum[16] in gas phase and the 0–0 original band was determined to be at 313.8 nm (31870 cm^{-1}). The adiabatic ionization energy of 1FN has been determined accurately to be 66190 cm^{-1} in our experiment by mass-analysed threshold ionization spectrum. For $(1\mathrm{FN})_2$ clusters, the resonant two-photon ionization (R2PI) spectrum[12] indicates that the first resonant electronic transition appears at about 315 nm (31746 cm^{-1}) with a relatively large linewidth near 2 nm, but its ionization energy is unknown. There is no information about other 1FN clusters. Many generic cluster properties (G), such as ionization energy, can be described by simple scaling laws as[1]

$$G(N) = G(\infty) + bN^{-1/3}, \quad (2)$$

where $G(\infty)$ is the value of property G in the bulk limit and N is the cluster size. Estimated by this law coarsely, the IFN cluster ionization energy would decrease as the increase of cluster size. Based on the above parameters, we selected UV laser with 281 nm (35587 cm^{-1}) as the ionization source which had high enough one-photon energy to excite 1FN monomers or 1FN clusters to higher densely electronic states and then the excited species to be ionized by absorbing another photon through "soft" ionization process. The scheme has the advantage of ionizing all the clusters with approximately equal efficiency, so the cluster distribution can be examined.

Figure 1 shows the TOF mass spectra of 1FN species with 20 μJ/pulse at different inlet pressures. By controlling the pulsed valve opening time, the inlet pressures can be changed easily and such changes can be simply monitored by the vacuum pressure in the ionization chamber. As the inlet pressure increases, from 1.3×10^6 Pa to 1.2×10^5 Pa, 1FN cluster ions appear gradually. It is clear that the intensity of 1FN cluster ions is much weaker than that of the 1FN monomer ions. At 1.2×10^5 Pa, the intensity of 1FN dimer ions has only about 10% of 1FN monomer ions. Meanwhile we notice that there are no fragments ions of 1FN appeared in the mass spectrum which imply that "soft" ionization condition might be fulfilled and the ions intensity distribution nearly responds the original distribution of the cluster generation.

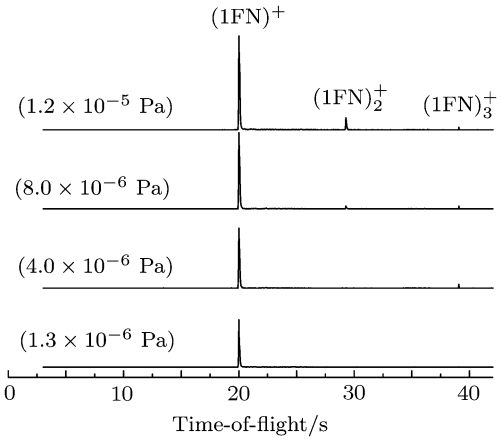


Fig. 1. Mass spectra of 1FN cluster ions obtained at different inlet pressures where the ionization laser is 281.0 nm with 20 μJ/pulse. Each mass spectrum is averaged with 300 times.

3.2. Effects of ionization laser fluxes to the cluster ions distribution

Keeping the inlet pressure to be 1.2×10^{-5} Pa, we show the mass spectra of 1FN cluster ions at different ionization laser fluxes in Fig. 2. In all cases, only three type ions, $(1FN)_n^+$ ($n = 1 \sim 3$), are observed in the mass spectra, and the signal intensity decreases as the cluster size increases. But as the laser flux increases, the intensity of $(1FN)_2^+$ is increases obviously while the intensity of $(1FN)_3^+$ only increases a little. Picking out the ratio between the intensity of $(1FN)_2^+$ and $(1FN)^+$, as shown in Fig. 3, the ratio keeps about 10% at lower laser flux and then increases quickly as laser flux increases even more. As the laser flux equals 60 μJ/pulse, the ratio reaches to 60%, while the trimer ion can still be neglected.

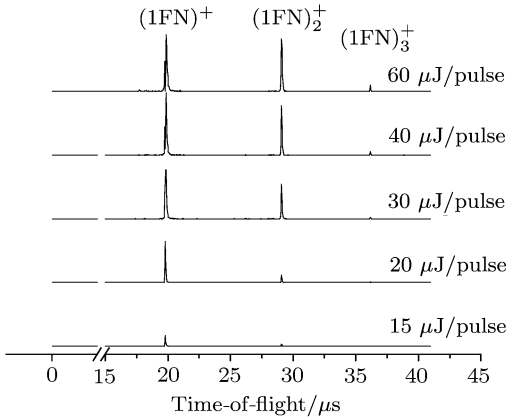


Fig. 2. Effects of ionization laser flux on the 1FN cluster ions distribution.

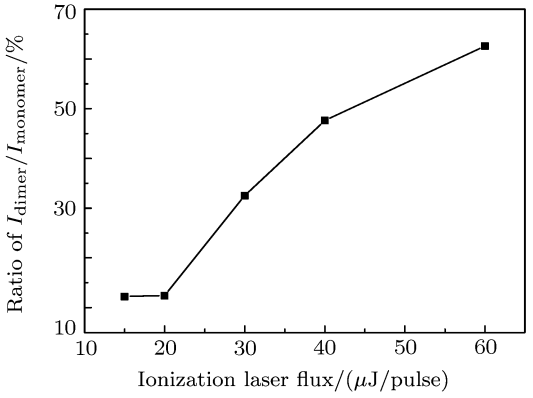


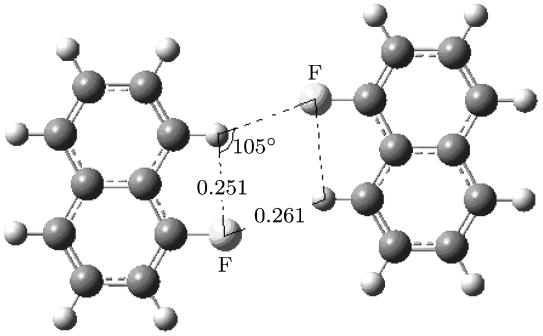
Fig. 3. Effects of ionization laser flux on the ratio between the intensity of 1FN dimer ions and monomer ions.

The ionization efficiency depends on the neutral cluster concentration as well as on the photon ionization cross section of each cluster, the latter is a function of the photon energy. In our experiment, fixed ionization laser at 281 nm is used and the inlet pressure is kept at 1.2×10^{-5} Pa, so the effects of laser flux on the mass spectra distribution can be mainly attributed to the non-linear effects of strong light interaction with 1FN species. At lower laser flux, "soft" ionization plays the dominating role and each species has nearly equal ionization efficiency, so the mass spectral distribution reflects the original jet-cooled neutral clusters producing results. Figure 2 shows that when the laser flux is lower than 20 μJ/pulse, the ratio keeps about at 10% as a constant. It is also reasonable that the 1FN monomers are dominant in the molecular beam by considering the relatively weak binding energies within 1FN clusters. As the laser flux increases to higher level, the non-linear effects during the cluster

ionization process may take a more important function, which break down the original cluster distribution in the mass spectrum. Of course, it is hard to give a detailed description about the variation of the mass distribution. However, based on the following calculations about 1FN dimer structures, we suggest that 1FN dimer just forms the first complete cluster shell which would play an important role for the stability distribution of the relatively stronger $(1FN)_2^+$ signals.

3.3. The DFT calculations of 1FN dimer structures and binding energies

We employ the Gaussian-03 suite of program[17] to investigate the most possible structures of 1FN dimer. All calculations were carried out within the premise of the density functional theory (DFT) using Becke's three-parameter hybrid functional[18] combined with the electron-correlation functional of Lee, Yang, and Parr (B3LYP).[19] The molecular geometry optimizations were made at 6-311++g(d,p) basis set levels and a planar geometric structure of 1FN dimer was obtained, as shown in Fig. 4, where two 1FN molecules are combined through two hydrogen bonds which conform between C–F and H–C. The two hydrogen bonds form a parallelogram where the hydrogen bond length is 0.261 nm. We also try to calculate the binding energy of the dimer, and the corresponding energies were corrected for basis set superposition error (BSSE) and higher order electron correlation effects by using counterpoise correction calculation.[20,21] But at the same basis set level, 6-311++g(d,p), calculations were stopped because of the unstability of diffuse functions. We reduced the basis level to 6-311+g(d), calculations were completed smoothly. At this level, we obtained the binding energy 2.22 kJ/mol (0.53 kcal/mol, 0.023 eV, 185 cm^{-1}). Comparing with typical hydrogen bond strengths in the range 10–25 kJ/mol, we find that the calculated binding energy is inclined to the low side. Accurate computation of weak intermolecular interactions such as the binding energy of large molecular dimers requires a high level of electron correlation and theoretical methods are developing.[22−24]



$E = -970.51596$ Hartree

Fig. 4. A probable geometric structure of $(1FN)_2$ combined with two hydrogen bonds. The numbers denote the bond lengths in nm units.

Calculations indicate the 1FN dimer structure shown in Fig. 4 having zero dipole moment, so such frame may be the smallest unit where the first "shell" is completely formed. Based on this unit, larger 1FN clusters could be produced by adding more 1FN molecules outside the first "shell". Comparing with other size 1FN clusters, we find that the 1FN dimer with two hydrogen bonds would have the largest binding energies, so in our experiment, the 1FN dimer ions have relatively intense signals.

4. Conclusions

The ionization of 1FN clusters under UV laser at 281 nm has been studied by using supersonic molecular beam with TOFMS. The effects of sample inlet pressures and ionization laser flux on mass spectral distribution have been discussed. A planar geometric structure of 1FN dimer was obtained by DFT calculation with B3LYP method at 6-311++g(d,p) basis set level, and the dimer is combined through two hydrogen bonds and forms the first "shell" as fundamental unit to induce more large clusters.

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