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One-colour resonant two-photon ionization spectrum of the 1-fluoronaphthalene dimer and *ab initio* calculation*

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The one-colour resonant two-photon ionization (R2PI) spectrum of the 1-fluoronaphthalene (1FN) dimer has been studied in the wavelength range of 304 to 322 nm by using a supersonic molecular beam and time-of-flight mass spectrometry. Compared with the original band 0_0^0 (at 313.8 nm) of the $S_1 \leftarrow S_0$ transition of the 1FN monomer, a red-shifted band was observed in the 1FN dimer spectrum at about 315 nm with a relatively large linewidth, nearly 2 nm. Based on the consideration of inductive effect and *ab initio* calculations, this red-shifted band is assigned to the first electronic excited transition of the 1FN dimer. A possible geometric structure of the 1FN dimer is also obtained with calculations that the two 1FN molecules are combined through two hydrogen bonds which are formed between the hydrogen atom of a molecule and the fluorine atom of a neighbouring molecule. A time-dependent calculation was also carried out and the results are consistent with the experimental data.

Keywords: 1-fluoronaphthalene dimer one-colour resonant two-photon ionization spectrum, 1FN dimer structure, *ab initio* calculation, time-dependent calculation

PACC: 3640B, 3120A, 8280M

1. Introduction

Aromatic molecular clusters combined via the van der Waals force or other weak bonds have been studied intensely from both experimental and theoretical points of view due to their importance in many physical and chemical phenomena.[1,2] The study of structures, energies, and intramolecular dynamics of mass-resolved clusters of aromatic molecules by resonant two-photon ionization mass spectrometry (R2PI/MS) provides a powerful means to investigate such interactions.[3−5]

Spectroscopic study of the 1FN molecule in the gas phase has mainly focused on the ground and the first electronic excited state. Singh and Thakur[6] studied the vapour phase absorption spectra of 1FN under high resolution; some vibronic bands were assigned where the original band 0_0^0 of the $A^1A' \leftarrow X^1A'$ transition is at 313.8 nm. The ionization energy of 1FN was determined to be 8.15 eV from photoelectron spectra with low resolution.[7] A significant number of experimental and theoretical studies for the naphthalene dimer have characterized the structures, photo ionization dynamics and reactions which happen in interclusters or intraclusters.[8−13] However, very few R2PI spectroscopic studies of dimers of mono-substituted naphthalene have been reported. In this paper, we report the one-colour R2PI experimental results of the jet-cooled 1FN dimer. The purpose of our effort is to understand the red-shift of the original band 0_0^0 of the 1FN dimer and the different spectral features compared with the 1FN monomer. Calculations for the 1FN dimer's structures, ionization energies, and binding energies are carried out to provide information to explain the experimental results.

2. Experiment and calculation methods

Experiments were performed with a time-of-flight mass spectrometer (TOF MS). The sample of 1-fluoronaphthalene (Aldrich, 99% purity, USA) was

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heated to about 110 °C to acquire sufficient vapour, then seeded into 10^5 Pa of helium and expanded into a standard vacuum chamber through a 0.15 mm diameter nozzle orifice of a pulsed valve (general valve series 9) which was operated at 10 Hz. The molecular beam was collimated by a skimmer located 15 mm downstream from the nozzle orifice. Two independent tunable UV laser systems were used for one-colour or two-colour R2PI spectrum experiments. A YAG laser (Quanta-Ray Lab-150) and a pumped dye laser (Sirah PRSC-G-18) with DCM, Rhodamine 590 and 610 dyes were employed. The output of the dye laser was doubled by a KDP/SHG crystal to produce UV radiation, and the final output with a typical pulse energy of 0.3–0.5 mJ/pulse was guided into the TOFMS chamber with a $f = 50$ cm spherical focus lens. The neutral molecules were ionized by the absorption of two UV photons of the appropriate wavelength, then the ions were extracted by a high-voltage pulse, and lastly detected by a dual microchannel plate (MCP) detector. The MCP signals were collected and analysed by a multichannel scaler (Stanford Research Systems, SR430) and each mass spectrum was averaged 300 times. The total timing sequence was controlled by a digital delay/pulse generator (Stanford Research Systems, DG 535).

The calculations were performed using the Gaussian 03W program package.[14] For the neutral ground state S_0 and cationic ground state D_0, the density functional theory (DFT) method with the 6-311++G(d,p) basis set was applied to predict the molecular properties including possible structures and energies. With the same basis set, the time-dependent DFT method was used to estimate the first electronic excited state S_1 energy. Based on these calculated results, the 1FN dimer's binding energy and ionization energy are obtained.

3. Results and discussion

3.1. R2PI spectrum of 1FN

The origin of the $S_1(A') \leftarrow S_0(A')$ electronic transition of 1FN lies at 313.8 nm (31870 cm^{-1}) just as the UV absorption spectra indicated[6] and the adiabatic ionization energy of 1FN has been determined accurately to be 66190 cm^{-1} in our experiment by the mass-analysed threshold ionization spectrum. So 1FN can be ionized by one-colour R2PI when the laser wavelength is less than 302.2 nm. But for obtaining the original band 0_0^0 transition and lower vibrational modes in the S_1 state, two-colour R2PI should be used in which the pump laser scans over the 303–318 nm (33003–31446 cm^{-1}) range and the ionization laser is fixed at 281.0 nm (35587 cm^{-1}). 1FN clusters can be produced at higher inlet pressures. To protect the 1FN monomer spectrum from contamination coming from the possible cluster dissociation after ionization, the ionization region was maintained at a pressure of 1.0×10^{-6} Pa, in which only $1FN^+$ was observed completely in the mass spectrum. Figure 1(a) shows the typical mass spectrum and Fig.1(b) presents the two-colour R2PI spectrum for the mass-selected 1FN monomer. It is clear that only sharp peaks are obtained where the strongest one corresponds to the original band and the others are related to the vibronic bands in S_1 state. Here we are not going to give a detailed discussion about the assignment of these vibrational modes.

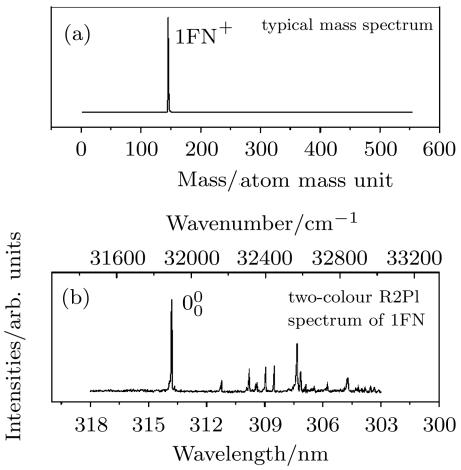


Fig.1. (a) Typical TOF mass spectrum of 1FN. The pressure in the ionization region is 1.0×10^{-6} Pa; (b) two-colour R2PI spectrum of 1FN. The pump laser scans over 303–318 nm and the ionization laser is fixed at 281.0 nm.

3.2. R2PI spectrum of 1FN dimer

A wide variety of species can be formed by collisional association in an adiabatic expansion of a high-pressure gas mixture through a nozzle into a vacuum. The molecules are associated via van der Waals forces or hydrogen bonds, greatly enriching the potential energy surface along both intra- and (the newly formed) inter-molecular vibrational coordinates. As the inlet pressure increases, the 1FN monomer, dimer, and very weak trimer of cluster ions can be observed in the mass spectrum even if only a one-colour laser is used and the laser wavelength is as long as 315 nm. The typical

mass spectrum is shown in Fig.2(a), the pressure in the ionization region being kept at about 5×10^{-6} Pa. Because one photon energy of 315 nm is lower than the 1FN 0_0^0 transition (313.8 nm) needed, this indicates that the dimer would have lower exciting and ionizing energies. To investigate the dimer's electronic exciting spectrum, we limit our laser scanning from 304.0 nm to longer wavelengths, which can eliminate the effect of 1FN monomer ionization by two-photon ionization. Figure 2(b) shows the one-colour R2PI spectrum of the 1FN dimer in the laser wavelength range of 304.0 to 322.0 nm; meanwhile the 1FN monomer spectrum in the same scan range is also picked out just by the mass-selected channel and put together with the 1FN dimer as a convenient comparison. Obviously, the spectrum of the 1FN monomer in Fig.2(b) is very similar to the spectrum of the 1FN dimer where only broad peaks can be observed and the lowest band appears at about 315 nm with nearly 2 nm of linewidth. It is certain that the spectrum of the 1FN monomer shown in Fig.2(b) is closely correlated with the 1FN dimer and it most probably comes from the dissociation of dimer ions during the ionization process.

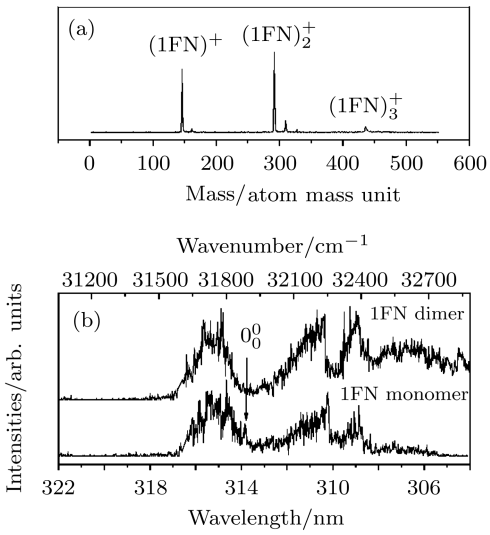


Fig.2. (a) Typical TOF mass spectra of 1FN cluster ions, (b) one-colour R2PI spectrum of 1FN monomer and 1FN dimer. The pressure in the ionization region is 5.0×10^{-6} Pa.

Several experiments on the R2PI spectrum of van der Waals clusters have shown that the original band 0_0^0 of the clusters usually has a red-shift as compared with the 0_0^0 band of corresponding monomers.[15] Considering the fact that the 0_0^0 band of 1FN is at 313.8 nm, we try to assign the lowest broadened peak appearing in the R2PI spectrum of the 1FN dimer at about 315 nm to the original 0_0^0 transition, and the others to the higher electronic vibronic transitions of the IFN dimer.

The red-shift and band broadening are the most obvious features of the spectrum of the 1FN dimer. The red-shift may be caused by inductive effects which are produced when two single molecules combine to form a dimer. The original band 0_0^0 of 1FN possibly corresponds to the transition of a π electron from the bonded conjugate orbitals of the aromatic ring to the anti-bonded conjugate orbitals, that is, $\pi* \leftarrow \pi$. For the dimer of 1FN, the two single 1FN molecules are mostly combined together through hydrogen bonds between C–F and another molecule's H atom. Such an H-bond formation may cause an inductive effect which leads to the change of distribution of π electron densities; in this way, the first electronic exciting energy of the dimer may be decreased as compared with that of the 1FN monomer. The following calculations for the excited state transition can also provide a guide to the estimation.

Several factors may be responsible for the peak broadening. (A) Nearly isoenergetic dimers and conformers exist simultaneously, which are produced in the beam in different ratios, depending on the expansion conditions. The relative shift of the first electronic exciting transition for each conformer may cause broadening of the 1FN dimer original band. (B) Large geometric changes happen in the excitation state. (C) Vibrational structure due to the excitation of intermolecular motion in the electronic excited state S_1 may appear in the spectrum even if the clusters are vibrationless in the ground state S_0. (D) A rare possibility comes from the dissociation of larger clusters even though only very few trimer ions are observed in the mass spectrum.

3.3. *Ab initio* and time-dependent calculations for the S_0 and S_1 states of the 1FN dimer

To predict the possible structures of the 1FN dimer, some calculations were carried out with the Gaussian03 program package.[14] Figure 3 gives the calculated result where one stable structure was obtained by using the DFT method at the 6-311++g(d,p) basis set level. The dimer is formed through two H-bonds with a bond length of 0.261 nm, and its structure has a C_{2h} symmetry. Of course, other possible conformers of the 1FN dimer might exist. However, the above one we obtained is the most

possible structure because it has the highest calculated binding energy. Based on this structure, the electronic transition energy as well as the ionization energy is also calculated. The results are listed in Table 1.

Table 1. Theoretical and experimental electronic transition energy, ionization energy, and binding energy of 1FN monomer and 1FN dimer.

species	energy/Hartree[a]	$S_1 \leftarrow S_0$ transition		binding energy	ionization energy	
		experiment	theory[b]		experiment	theory[a]
1FN	–485.2573	313.8 nm	293.81 nm		66190 cm^{-1}	64180 cm^{-1}
			(4.2199 eV)		(8.2065 eV)	(7.9567 eV)
$(1FN)_2$	–970.5160	315.0 nm	310.22 nm	0.03571 eV		60020 cm^{-1}
			(3.9967 eV)			(7.4415 eV)
$1FN^+$	–484.9649					
$(1FN)_2^+$	–970.2425					

[a]Calculated with DFT method at 6-311++G(d,p) basis set level.
[b]Calculated with time-dependent DFT method at 6-311++G(d,p) basis set level.

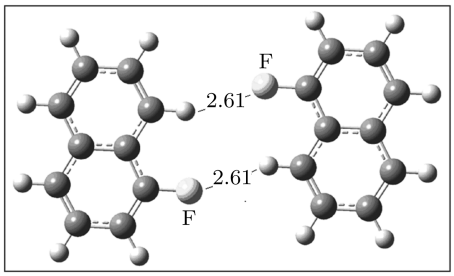


Fig.3. A possible stabilized structure of the 1FN dimer calculated by means of the DFT method at the 6-311++g(d,p) basis set level. The numbers denote the bond lengths in angstrom units.

The first electronic transition energy of the 1FN dimer was calculated by using the time-dependent DFT method. The results show that the first electronic transition energy and ionization energy of the 1FN dimer are 3.9967 and 7.4415 eV, which are lower than those of the monomer 4.2199 and 7.9567 eV, respectively. So it is reasonable that the 1FN dimer could be ionized by R2PI with about a 315 nm laser while the 1FN monomer cannot be ionized (it needs 3 photons).

The calculated binding energy of the dimer is 0.03571 eV, as listed in Table 1, but we think there may be some errors because the binding energy is simply obtained by $\Delta E = 2E(1FN)\text{-}E(\text{dimer})$, where the E_s are the single point energies calculated at the B3LYP/6-311++G(d,p) basis set level. Usually, to obtain more accurate binding energies it is necessary to consider the basis set superposition error (BSSE) correction. Unfortunately, we have made some efforts at such calculations, but did not obtain final results because such calculations cannot be processed smoothly or paused with some unknown reasons.

4. Conclusions

The first electronic excitation transition of the 1FN dimer has been studied with the R2PI spectrum in the laser wavelength range of 304 to 322 nm, and the original band 0_0^0 is obtained at about 315 nm. The spectral features are displayed as a broadened band, which can be explained as the results of rotational profile broadening and nearly isoenergetic conformations. A possible stable structure of the dimer, which is formed with two H-bonds, is calculated by means of the DFT method at the 6-311++g(d,p) basis set level, and the calculated results are in qualitative agreement with the experimental results.

Acknowledgments

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