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One-photon and Two-photon Ionization Threshold Spectra of Jet-cooled 1,4-Difluorobenzene

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Ionization thresholds of jet-cooled 1,4-difluorobenzene were measured by one-photon ionization and two-photon ionization from the S_1 state. Most of the ionization thresholds were commonly observed in both threshold spectra in spite of the existence of inversion symmetry for this molecule. It is concluded that the symmetry of ejected photoelectron changes in the one-photon and two-photon ionizations leaving the symmetry of the cation unchanged.

Two-color ionization threshold spectroscopy is a powerful tool to study the vibrational structure of a cation.[1] It also enables us to determine the accurate ionization potential of a neutral molecule. Briefly, this technique uses two tunable dye lasers (see Fig. 1a). A sample molecule in a supersonic jet is excited to S_1 state by the first laser ν_1. Then, the S_1 molecule is further excited by the second laser ν_2. Monitoring ion current, the second laser is scanned in frequency. When the sum energy of ν_1 and ν_2 just exceeds the ionization potential, the ion current is generated because of the ionization of the molecule. Consequently, the ionization potential is given by the ionization threshold whose position can be determined with an accuracy of the laser resolution (Fig. 1b). Ionization threshold also appears when $\nu_1+\nu_2$ reaches a vibrational level of the cation. Therefore, we can obtain the vibrational frequencies of the cation from the observed thresholds. Furthermore, the height of the ionization threshold is determined by Franck-Condon factor between the S_1 state and the electronic state of the cation, so we can discuss the structure of the cation from the observed heights.

Present work is an extension of our previous study on the one-photon ionization threshold spectrum of jet-cooled 1,4-difluorobenzene (p-DFB).[2] The one-photon ionization threshold spectrum of the S_1 molecule has been reported there as shown in Fig. 2a. It is also possible to measure the two-photon ionization threshold spectra by using the photon of half energy as illustrated in Fig. 1c. A comparison between the one-photon and two-photon threshold spectra is the subject of the present paper. The comparison enables us to examine mutual exclusion rule for the ionization process. For a molecule having inversion symmetry, $\nu_1+2\nu_2$ transition has

$u \leftrightarrow g$ selection rule, while $\nu_1+\nu_2$ has $g \leftrightarrow g$ (or $u \leftrightarrow u$). Therefore, the final state of the $\nu_1+2\nu_2$ transition should be different from that of the $\nu_1+\nu_2$ transition. However, in the case of ionization, we have to take into account of the symmetry of an ejected electron in addition to the symmetry of the core ion. The symmetry of the photoelectron has g or u symmetry depending on its even or odd angular quantum number, respectively. Thus, we can discuss the nature of the ejected photoelectron from the comparison of the one-photon and two-photon threshold spectra. Information on the nature of the photoelectron can also be obtained from traditional photoelectron spectroscopy. However, it has no enough resolution to resolve vibrational levels of polyatomic cations.

Experimental apparatus has been described elsewhere.[2] Briefly, output of a XeCl excimer laser was split into two to pump two dye lasers. Output of the first dye laser light was frequency doubled by a SHG crystal (BBO or KDP) and was used as ν_1. p-DFB molecule in a supersonic jet was excited to a specific level in the $S_1{}^1B_{2u}$ state by ν_1. The second dye laser light ν_2 was coaxially introduced into a vacuum chamber from the opposite direction to ν_1 and ionized the S_1 molecule. The ions generated by $\nu_1+2\nu_2$ were introduced into a detector chamber by a repeller with an appropriate voltage (typically 10V/cm). The ions were detected by a channel multiplier (Murata Ceratron) and the ion signal was amplified by a current amplifier (Keithley 427). The amplified signal was integrated and was recorded as a function of laser wavelength by a digital boxcar integrator system (PAR4402/4420).

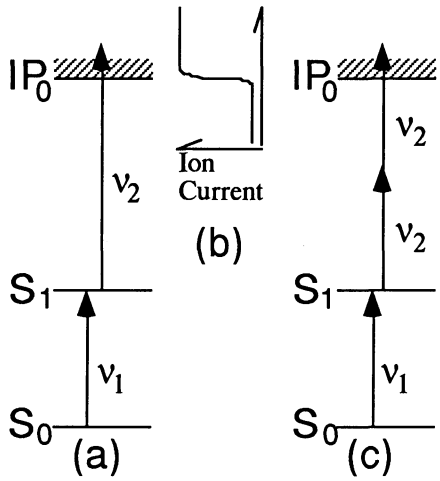

Fig. 1. Schematic diagrams showing the principle of one-photon ionization threshold spectroscopy (a), and that of two-photon ionization threshold spectroscopy (c) from S_1 state. Schematic threshold spectrum was also shown in Fig.1(b).

Figure 2 shows a) the one-photon ionization threshold spectrum and b) the two-photon ionization threshold spectrum of jet-cooled p-DFB. The former is essentially the same as that reported in a previous paper.[2] Both spectra were obtained after exciting p-DFB to the S_1 origin (36840 cm^{-1}) by the first laser ν_1 and were drawn for total energies of the transition ($\nu_1+\nu_2$ for Fig. 2a and $\nu_1+2\nu_2$ for Fig. 2b). Several sharp ionization thresholds were found in both spectra. In the one-photon ionization threshold spectrum, the lowest ionization threshold (73871 cm^{-1}) is assigned to the adiabatic ionization threshold (IP_0; the zero vibrational level of the ground state cation). The thresholds lying above IP_0 are the vertical ionization thresholds which correspond to the vibrational levels of the cation 6_1 (444 cm^{-1}), 5_1 (798 cm^{-1}), 4_1 (1197 cm^{-1}), and their combinations, as shown in the figure.[2, 3] The spectral resolution for the ionization threshold is ± 5 cm^{-1}.

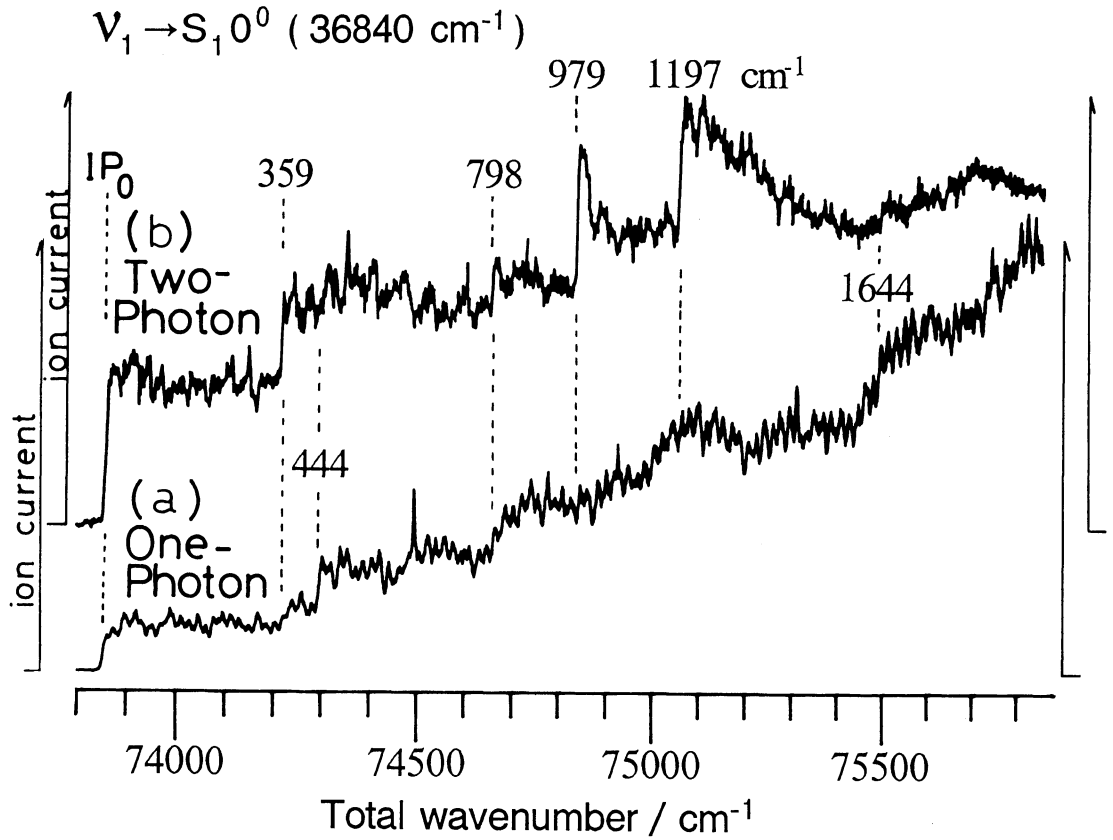

Fig. 2. a) One-photon ionization threshold spectrum and b) two-photon ionization threshold spectrum of jet-cooled 1,4-difluorobenzene (p-DFB). Both spectra were obtained after exciting molecule to S_1 origin (36840 cm^{-1}) by ν_1, and were drawn for $\nu_1+\nu_2$ and $\nu_1+2\nu_2$ wavenumber for one-photon (a) and two-photon ionization threshold spectrum(b), respectively. The spectral resolution for the ionization threshold was ± 5 cm^{-1}.

The two-photon ionization threshold spectrum (Fig. 2b) also shows several ionization thresholds. IP_0 at 73871 cm^{-1} is also observed in the two-photon ionization threshold spectrum, and vertical ionization thresholds lying at IP_0 + 798 cm^{-1}, 1197 cm^{-1}, and 1644 cm^{-1} are identical to those in the one-photon ionization threshold spectrum. The correspondence is shown by broken lines in the figure. However, there exists apparent difference between the two spectra. Sharp thresholds at IP_0+359 and IP_0+979 cm^{-1} appearing in the two-photon spectrum are very weak or absent in the one-photon ionization spectrum. Contrary, a threshold at 444 cm^{-1} is prominent in the one-photon spectrum but not in the two-photon spectrum. The fact that most of the ionization thresholds were commonly observed in both spectra can be explained by a symmetry reduction of molecular structure in S_1 and/or in the ground state cation. However, for the S_1 state of p-DFB, the molecular structure has been already established to be D_{2h}.[4-6] For the p-DFB cation, molecular structure was suggested to be distorted from the analysis of Rydberg series.[2] However, the distorted structure should maintain inversion symmetry because only s- and d-Rydberg series converging to IP_0 were observed in the transition

from the S_1 origin. Thus the symmetry reduction of the molecular structure is not responsible for the common appearance of the thresholds.

Consequently, the reason for the common appearance of the threshold must be ascribed to the symmetry of the ejected photoelectron. If the symmetry of the photoelectron is different in the one-photon and two-photon ionization keeping the same symmetry for the cation, it is possible to explain the common appearance of the threshold. Since both spectra show the clear IP_0 threshold, the ionization continuum which is described by the product of the wavefunction of the cation and that of the photoelectron must have the symmetry allowed from the S_1 state (B_{2u}). The allowed symmetry from the S_1 state are A_g, B_{1g}, and B_{3g} for the one-photon ionization, and A_u, B_{1u}, B_{2u}, and B_{3u} for the two-photon ionization. The symmetry of the ejected photoelectron can be characterized in terms of the symmetry of the cation.[7] Then, the symmetry of the photoelectron must be b_{1g}, b_{2g}, or b_{3g} for the one-photon ionization from S_1, and a_u, b_{1u}, b_{2u}, or b_{3u} symmetry for the two-photon ionization. The former corresponds to d-wave, while the latter is p-wave. Since s-wave has a_g symmetry, no s-wave is expected in both ionization processes. The observed difference for several thresholds mentioned above is probably not an essential difference. The strong appearance of the thresholds of IP_0+359 and IP_0+979cm^{-1} in the two-photon spectrum is interpreted as due to the enhancement of the threshold intensity by resonance with higher excited states lying near the $\nu_1+\nu_2$ region.

In summary, the two-photon ionization threshold spectrum from the S_1 origin was measured for jet-cooled p-DFB. From the comparison with the one-photon ionization threshold spectrum, it was concluded that the d-electron is ejected in the one-photon ionization and the p-electron in the two-photon ionization.

References

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