



Determination of the accurate ionization energy and cationic structure of cyanopyrazine by one-photon mass-analyzed threshold ionization spectroscopy



Do Won Kang, Hong Lae Kim*, Chan Ho Kwon*

Department of Chemistry and Institute for Molecular Science and Fusion Technology, College of Natural Sciences, Kangwon National University, Chuncheon 200-701, Republic of Korea

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ABSTRACT

The ionization energy and cationic structure of cyanopyrazine have been determined for the first time by pulsed-field threshold ionization mass spectrometry. The ionization energy was accurately measured to be $80,305 \pm 6 \text{ cm}^{-1}$ ($9.9566 \pm 0.0007 \text{ eV}$) from the 0-0 band position in the mass-analyzed threshold ionization (MATI) spectrum obtained for the direct $S_0 \rightarrow D_0$ transition using a vacuum ultraviolet laser pulse generated by four-wave mixing in Kr. The highest occupied molecular orbital (HOMO) and singly occupied molecular orbital (SOMO) calculations indicated the extent of conjugation of nonbonding orbitals on nitrogen atoms with the π orbital in cyanopyrazine, and clarified the effect of substitution of H with CN in pyrazine on the ionization energy of cyanopyrazine. The observed MATI spectrum was interpreted using the Franck-Condon factors and vibrational frequencies calculated through adjustment of the geometrical parameters of the cyanopyrazine cation in the ground electronic state at the B3LYP/cc-pVTZ level. From rigorous analyses, it has been concluded that upon ionization, the cyanopyrazine cation in the D_0 state should retain a planar structure with C_s symmetry, similar to the ground state molecule.

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1. Introduction

Great interest in studying the molecular cations formed in many chemical reactions as well as existing in the interstellar medium have given rise to distinct experimental approaches, which could provide information on the ionization energies as well as electronic and vibrational states of the cations. Particularly, many such studies have been carried out using photoionization mass spectrometry and photoelectron spectroscopy, which start with the molecular form of the cation of interest [1]. Generally, the ionization energies of polyatomic molecules can be measured by photoelectron spectroscopy, where the spectra provide information on the electronic and vibrational structures of the cations of some small molecules [2]. In addition, combination of the results of these studies with molecular orbital-based theoretical calculations has provided novel structural information on the cations. However, precise measurement of the vibrational frequencies to determine the accurate molecular structure of the cation has been hindered by the poor

energy resolution of the electron monochromator. The technique of field ionization uses high-resolution lasers to scan through the Rydberg states of a molecule, which converge to the cationic state and thus afford the ionization energy. The method allows the measurement of the ionization energies and vibrational frequencies of the cation with higher precision than conventional photoionization mass spectrometry. Through delayed extraction of the threshold photoelectrons from molecules in the Rydberg state, zero kinetic energy (ZEKE) spectroscopy can also measure the high-resolution vibrational spectra of polyatomic cations [3–5]. Instead of detecting electrons, molecular ion detection using a mass spectrometer can provide the vibrational spectrum of a cation of designated mass with a resolution similar to that of ZEKE. Ever since it was first reported, mass-analyzed threshold ionization (MATI) spectroscopy has proven to be one of the most powerful techniques for measuring the high-resolution vibrational spectra of polyatomic cations, from which the accurate ionization energies and molecular structures of the corresponding cations can be determined [6].

In normal MATI spectroscopy, the lasers are tuned to the Rydberg states through an intermediate state because the first ionization energies of most polyatomic molecules fall between 8 and 12 eV, which is currently inaccessible using commercial VIS/UV lasers. This two-photon absorption to reach the Rydberg states can

* Corresponding authors. Tel.: +82 332508496.

E-mail addresses: hkim@kangwon.ac.kr (H.L. Kim), chkwon@kangwon.ac.kr (C.H. Kwon).

be achieved using two lasers of different colors, with the first laser tuned to a specific vibronic intermediate state and the second laser scanning through the Rydberg states; this is the so-called $1+1'$ MATI scheme. The observed spectra are interpreted according to the selection rules based on the molecular structures where the electronic transitions take place. In order to correctly assign the peaks in the observed MATI spectrum, the first transition to the intermediate state, which is the origin of the second transition to the Rydberg states, must be clearly characterized. Unfortunately, most polyatomic molecules in electronically excited states undergo structural changes as well as various rapid photophysical and photochemical processes, resulting in ambiguous vibronic structures in the spectra, which makes proper selection of the intermediate state difficult. Because of these difficulties, the MATI spectra of some small molecules, in favorable cases, have been observed and interpreted using the $1+1'$ scheme [7–11].

The one-photon vacuum ultraviolet MATI (VUV-MATI) technique was developed to avoid these difficulties and to excite the molecule to the Rydberg state by direct one-photon absorption, wherein an intermediate state is not necessary and a simple selection rule can be applied to assign the peaks in the MATI spectrum [12]. The vibrational spectra and structures of many polyatomic molecular cations have been investigated so far using the VUV-MATI technique [13–17]. However, a major drawback of VUV-MATI is the generation of coherent VUV radiation with a wide range of tunability and with enough power to detect ions in the mass spectrometer. VUV radiation with an energy of 9–10 eV can be produced by third harmonic generation or four-wave mixing in a nonlinear medium such as Kr gas, whereas different nonlinear media are required for producing VUV radiation with other energies [18,19].

Heterocyclic N-containing molecules such as pyrazine and pyrimidine have attracted much attention because they undergo vigorous photophysical processes upon electronic transitions such as vibronic coupling, which can be thoroughly investigated by both experimental and theoretical approaches. The high-resolution laser-induced fluorescence spectra of pyrazine and pyrimidine were measured, based on which the eigenstates on S_1 were characterized [20–23]. The rate of S_1-T_1 intersystem crossing in pyrazine, measured by time-resolved photoelectron imaging spectroscopy, was in the range of tens of picoseconds [24]. These molecules have been classified as intermediate-case molecules in terms of intramolecular vibrational energy redistribution (IVR) arising from vibronic couplings [25]. In addition to the studies on electronically excited states, ionization of these molecules has also been performed [7,8,26]. For example, the first ionization of pyrimidine can be achieved by removal of an electron from a nonbonding orbital on N, whereas the occupied, delocalized π orbitals in the ring have lower energy. Thus, upon ionization, the molecular structure of the corresponding ions would change slightly, especially on the N-site of the ring. Recently, the one-photon VUV-MATI spectra of pyrimidine and pyridine were obtained and the structures of the corresponding molecular ions were precisely determined by the so-called Franck–Condon fit [27,28]. Substitution of H by an electron donating or withdrawing group such as $C\equiv N$, may alter the molecular orbital structure and energies, resulting in changes in the ionization energies and certainly the structures of the cations.

In this study, the vibrational spectrum of the cyanopyrazine cation has been obtained for the first time by one-photon VUV-MATI mass spectrometry. The accurate adiabatic ionization energy and ground state structure of the molecular ions are determined using density functional theory (DFT) calculations for the structures and vibrational frequencies of cyanopyrazine in the S_0 and D_0 states and using Franck–Condon factor calculations for the $S_0 \rightarrow D_0$ transition.

2. Experiments

The experiments were performed using a home-built VUV-MATI spectrometer composed of a molecular beam chamber, a pulsed-field ionization time-of-flight (TOF) mass spectrometer, and a gas cell for VUV radiation generation, which are described in detail elsewhere [27,28]. The experiment, including modification of the ion source assembly, will be briefly summarized here. Cyanopyrazine was purchased from TCI (97%) and used without further purification. The seeded molecular beam was generated by expanding the vapor from a liquid heated in a reservoir at 100 °C through a pulsed nozzle (Parker Valve, 500 μm dia.) with a He stagnation pressure of ~ 3 atm. The molecular beam was introduced to the ionization chamber of the TOF mass spectrometer through a skimmer (Beam Dynamics, 1 mm dia.) located 3 cm downstream of the nozzle orifice, and the beam overlapped with the VUV radiation between the electrodes in a counter-propagated manner.

Coherent VUV radiation tunable in the 123–125 nm range was generated by four-wave difference frequency mixing in Kr gas via the Kr $5p[1/2]_0 - 4p^6$ resonance at 212.556 nm. The 212.556 nm light was generated using a barium borate crystal by mixing after doubling the 637.8 nm light from a dye laser (Continuum ND 6000) pumped using a Nd:YAG laser (Continuum Surelite II). Subtraction of the 720–770 nm light from another Nd:YAG laser-pumped dye laser (Shira PrecisionScan-LG) from two photons of 212.556 nm light in the Kr cell generates the tunable VUV radiation. The VUV radiation was separated from the residual UV and VIS radiation and introduced to the center of the ionization chamber. A gold plate was placed in the path of the VUV beam as a power monitor, and its output was used to normalize the intensity of each vibrational peak in the MATI spectrum. The dye laser output wavelengths were calibrated based on the optogalvanic effect in a Fe/Ne hollow cathode lamp, whose precision was $\pm 0.5 \text{ cm}^{-1}$ in the visible region.

A very-low pulsed-field ionization (PFI) voltage and dual stage extraction are needed for improving the spectral resolution of the VUV-MATI spectrum and achieving first-order focusing of the MATI ions initially generated with the spatial distribution. Hence, an ion source consisting of four electrode plates with rectangular slots was placed instead of the previously used three-electrode assembly with circular apertures (Jordan TOF products, C-677) [28]. In our new ion source, the first stage applies the PFI voltage, and the next achieves first-order spatial focusing of the generated MATI ions. The new electrode assembly and pulsing scheme simultaneously enhanced the spectral resolution ($\sim 13 \text{ cm}^{-1}$) and size of the MATI signal. A spoil field of 0–0.2 V cm^{-1} was applied in the ionization region to remove the prompt background ions. For the PFI, an electric field of 6–25 V cm^{-1} was applied $\sim 20 \mu\text{s}$ after the VUV laser pulse. Then, the generated MATI ions were extracted from the dual stage for first-order spatial focusing, flown through a field-free region, and detected by a dual microchannel plate (MCP) detector. An AC-type scrambling field was applied during laser irradiation, which significantly lengthened the lifetime of the molecules in the high n, l Rydberg states. The MATI spectrum was obtained by integration of the mass signal of the parent molecular ion ($C_5H_3N_3^+$) and corrected for variations in VUV laser intensity.

All quantum chemical calculations were carried out at different DFT levels (viz. B3LYP, B971, and B2PW91) with various basis sets using the Gaussian 09 program package [29]. The basis set size was increased to aug-cc-pVTZ for basis set convergence. Then, to analyze the MATI spectrum, which is essentially the vibrational spectrum of the molecular cation, calculation of the Franck–Condon factors using the geometries, vibrational frequencies, and normal mode eigenvectors for cyanopyrazine and the cation in the ground electronic state were performed at the B3LYP/cc-pVTZ level with

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