Active vibrations of 1-cyanonaphthalene cation studied by mass-analyzed threshold ionization spectroscopy

Vidya Shivatare [a,b,c], Sheng Yuan Tzeng [a], Wen Bih Tzeng [a,d,*]

[a] *Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-166, 1 Section 4, Roosevelt Road, Taipei 10617, Taiwan*
[b] *Taiwan International Graduate Program, Department of Chemistry, National Tsing Hua University, Taiwan*
[c] *Academia Sinica, 128 Academia Road, Section 2, Nankang, Taipei 115, Taiwan*
[d] *Department of Chemistry, National Taiwan Normal University, 88, Section 4, Tingzhou Road, Taipei 11677, Taiwan*

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A B S T R A C T

We apply the two-color resonant two-photon mass-analyzed threshold ionization (MATI) spectroscopic technique to record the cation spectra of 1-cyanonaphthalene via four intermediate vibronic levels. The adiabatic ionization energy is determined to be $69\,466 \pm 5$ cm^{-1}. The distinct bands at 416, 472, 516, 669, and 852 cm^{-1} result from in-plane ring deformation vibrations of the cation. Analysis of these MATI spectra suggests that the molecular geometry and vibrational coordinates of the observed vibrations of the cation in the ground D_0 state resemble those of the neutral in the electronically excited S_1 state.

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1. Introduction

Due to their versatile applications in pharmaceutical and chemical industries, naphthalene and its derivatives have been extensively studied by spectroscopists [1–6]. 1-Cyanonaphthalene having a cyano (or nitrile) substituent is a basic ingredient in synthesizing antifungal agents used in the treatment of dermatocytes [7,8]. Many molecular properties of 1-cyanonaphthalene and its complexes have been investigated by using the laser-induced fluorescence (LIF), mass-selected resonance-enhanced two-photon ionization (R2PI), infrared-ultraviolet (IR-UV) double resonance and other spectroscopic methods and theoretical calculations [9–14]. Results from these studies have increased our knowledge about the geometry, vibrational energy, life time, rotational constant, and excimer formation of this molecule in the ground S_0 and electronically excited S_1 states. The ionization energy (IE) of 1-cyanonaphthalene has been reported [15,16]. However, the detailed spectroscopic data of this molecule in the ionic state are still not available in the literature. Both the zero-kinetic energy (ZEKE) photoelectron [17,18] and mass-analyzed threshold ionization (MATI) spectroscopic [19–21] techniques can provide information about the precise IE and active cation vibrations in the D_0 state. Because 1-cyanonaphthalene can form complexes or clusters under normal experimental conditions [9,10,14], we adopt the two-color (2C-) R2PI and MATI techniques for the present studies to avoid spectral congestion caused by impurities, complexes, and clusters.

In this Letter, we report the cation spectra of 1-cyanonaphthalene, recorded by ionizing through four different intermediate vibronic levels. Comparing the obtained experimental data with those of naphthalene [4] and some mono-substituted naphthalene derivatives [5,6], we can learn the substitution effect of the cyano group on the transition energy and molecular vibration.

2. Experimental and computational methods

2.1. Experimental method

All of the experiments reported here were performed by using a photoionization time-of-flight (TOF) mass spectrometer with two independent tunable UV lasers [22]. 1-Cyanonaphthalene (98% purity) was purchased from Sigma–Aldrich and used without further purification. The sample was heated to about 80 °C to acquire sufficient vapor pressure. The vapors were seeded into 2–3 bar of helium and expanded into the vacuum through a pulsed valve with a 0.15 mm diameter orifice. The free jet passed through a skimmer (1.0 mm diameter) located about 10 mm from the nozzle orifice. The skimmed molecular beam was intersected perpendicularly with two counter-propagating laser beams in the laser-molecular beam interaction zone which is at about 50 mm downstream from the nozzle orifice. During the experiments, the gas expansion, laser-molecular beam interaction, and ion detection regions were maintained at a pressure of about 1×10^{-3}, 1×10^{-5}, and 1×10^{-6} Pa, respectively.

In the MATI experiments, both the prompt ions and the Rydberg neutrals were formed simultaneously in the laser-molecular beam interaction zone. A pulsed electric field of -1 V/cm in this region was switched on about 40 ns after the occurrence of the laser

pulses to guide the prompt ions towards the opposite direction of the flight tube. In this way, the prompt ions were not detected by the particle detector. Because the Rydberg neutrals were not affected by the electric field, they kept moving to the second TOF lens region. About 11.8 μs later, a second pulsed electric field of +200 V/cm was applied to field-ionize the Rydberg neutrals. These threshold ions were then accelerated by the same electric field and passed through a field-free region before being detected by a dual-stacked microchannel plate detector. Mass spectra were accumulated at 1.2 cm^{-1} spacing for 300 laser shots. Composite optical spectra of intensity versus wavelength were then constructed from the individual mass spectra.

2.2. Computational method

We performed ab initio and density functional theory (DFT) calculations by using the GAUSSIAN 09 package [23]. These calculations predict the molecular geometries, total energies, vibrational frequencies, and many molecular properties in the S_0, S_1, and D_0 states. The fully optimized structures, total energies and vibrational frequencies in the S_0, S_1, and D_0 states were predicted at the restricted Becke three-parameter functional with the PW91 functional (B3PW91), time-dependent (TD)-B3PW91, and unrestricted B3PW91 calculations with the 6–311++G(d,p) basis set, respectively. In addition, the Hartree–Fock (HF), configuration interaction singles (CIS), and Becke three-parameter functional with the Lee–Yang-Parr functional (B3LYP) calculations were also performed. They give a spin multiplicity $< S^2 >$ of about 0.75 for the cation. The adiabatic IE was deduced from the difference in the zero-point energies (ZPEs) of the cation in the D_0 state and the neutral in the S_0 state.

3. Results

3.1. Vibronic spectrum

In consideration of the reported experimental values of the first electronic excitation energy and the IE [12,16], we have recorded the vibronic spectrum of 1-cyanonaphthalene by scanning the frequency of the excitation laser while fixing the ionization laser at 262.57 nm (38.085 cm^{-1}). As shown in Figure 1, the band origin of the $S_1 \leftarrow S_0$ electronic transition (E_1) appears at 31 412 ± 2 cm^{-1} which is in excellent agreement with previously
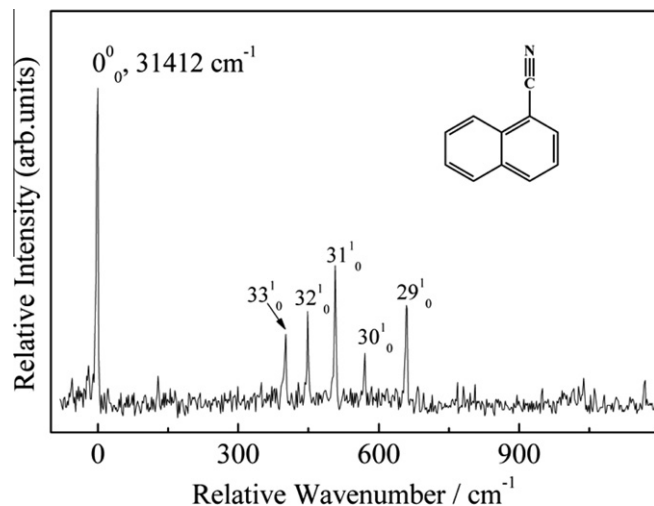
Table 1
Observed bands (in cm^{-1}) in the vibronic spectrum of 1-cyanonaphthalene.[a]

Ref. [9]	This work			Assignment approximate description[b,c]
	Exp.	CIS	TD-B3PW91	
404	402	401	399	33_0^1 , β(CCC)
454	448	459	461	32_0^1 , β(CCC) [$\overline{8}_0^1$]
510	507	504	499	31_0^1 , β(CCC) [9_0^1]
	571	585	578	30_0^1 , β(CCC)
663	659	645	648	29_0^1 , breathing [8_0^1]

[a] The experimental values are shifts from the 0_0^0 band at 31 412 cm^{-1}, whereas the calculated ones are obtained from the CIS (scaled by 0.90) and TD-B3PW91 (scaled by 0.96) calculations using the 6–311++G(d,p) basis set.

[b] The numbering of the normal vibrations follows Mulliken's convention [24] for 1-cyanonaphthalene, whereas symbols in square brackets are used by Rentien and coworkers [11] for naphthalene.

[c] β, in-plane bending.

reported values [9,11,12,14]. Within the entire spectral range, the largest excess energy is no more than 1250 cm^{-1}. Under these experimental conditions, only one peak corresponding to the 1-cyanonaphthalene ion appears in the TOF spectrum. Therefore, the quality of our vibronic spectrum by using the 2C-R2PI technique is better than that reported previously [14]. The spectral assignment is accomplished by comparing these experimental data with those of naphthalene [4], trans-1-naphthol (also called trans-1-hydroxynaphthalene) [5], and 1-fluoronaphthalene [6] as well as the predicted values from our theoretical calculations, as shown in Table 1. The numbering system of the normal vibrations of 1-cyanonaphthalene follows Mulliken's convention [24]. In addition, the symbols in square brackets are in accordance with Stockburger's classification for naphthalene [25], as those used by Rentien and coworkers [11]. The totally symmetric (a_g) modes are denoted by their numbers alone and b_{1g} modes by numbers with bars over
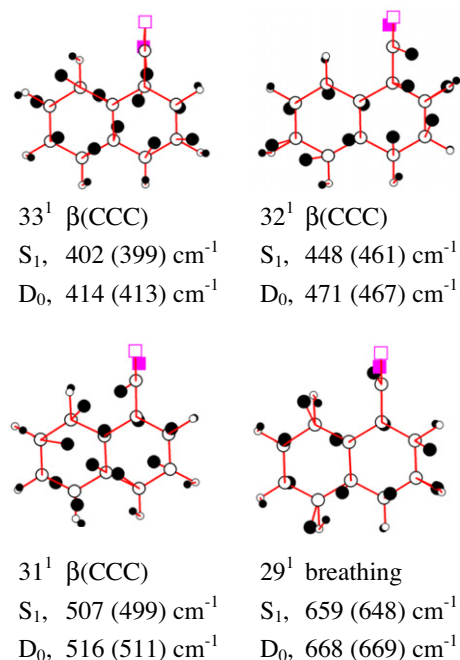

Figure 1. Vibronic spectrum of the $S_1 \leftarrow S_0$ electronic transition of 1-cyanonaphthalene.

Figure 2. Some observed active vibrations of 1-cyanonaphthalene in S_1 and D_0 states. The open circles designate the original locations of the atoms, whereas the solid dots mark the displacements. The measured and calculated (in the parentheses) frequencies are included for each mode. The predicted values are obtained from the TD-B3PW91 and UB3PW91 calculations with the 6–311++G(d,p) basis set for the S_1 and D_0 states, respectively, as shown in Tables 1 and 2.