

# A characterization of vibrationally excited $\text{NO}_2^+$ by ZEKE high-resolution threshold photoionization spectroscopy

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## INTRODUCTION

In addition to energetic reference points, statistical rate theory models for combustion systems require information to accurately calculate the state densities of reacting species. At chemically significant energies, anharmonicities play an important role in determining the distribution of vibrational levels, especially for weakly bound free-radical intermediates. Furthermore, free-radical reactions often encounter low-barriers, and in such cases, details in the anharmonic coupling of vibrational modes can affect dynamical outcomes, including the disposal of excess energy in products. Few experiments provide direct information, and model calculations must rely on theoretical potentials in order to estimate higher-order terms in vibrational force fields. Spectroscopic measurements provide an important means to test the validity of ab initio calculations.

Some time ago, we characterized the anharmonic terms in the vibrational potential of  $\text{NO}_2^+$  that give rise to bend-stretch Fermi resonance [1]. Using ionization-detected two-photon absorption, we obtained the spectrum of a long progression of vibrationally excited levels in the  $3p\sigma^2\Sigma_u^+$  Rydberg state of  $\text{NO}_2^+$ . The linear  $\text{NO}_2^+$  core of this Rydberg state possesses a vibrational potential that parallels the potential surface of the cation, so that the broad envelope of Franck-Condon factors for transitions from the bent neutral ground state provides a convenient means to observe cation vibrational structure over a wide energy range. Using a comprehensive fit to fifteen band positions through the (040)-(120)-(200) triad, we were able to estimate harmonic frequencies, diagonal anharmonicities and the cubic force constant,  $k_{122}$ . Three-color triple-resonant state-selected ionization experiments with ZEKE threshold photoelectron detection provided a direct measure of cation frequencies for comparison [2]. We found that the degree of vibrational coupling in the cation compares with the more extensively characterized  $3p\sigma$  Rydberg state. The experimental results for the core cation agree well in both cases with CCSD(T)/[4s3p2d1f] ab initio calculations including Fermi resonance effects.

We have now begun work seeking to test this potential by extending ZEKE measurements of cation vibrational structure to higher energy levels, reached in direct VUV transitions from the neutral ground state. To obtain these spectra, we have used the multipurpose photoelectron-photoion apparatus on the Chemical Dynamics Beamline at the Advanced Light Source.

Like the Rydberg spectrum, the spectrum of photoionizing transitions from the bent ground-state neutral to the linear cation forms long vibronic progressions. This displaced Franck-Condon envelope makes the adiabatic threshold difficult to discern, but does provide a very effective means

to explore the higher vibrationally excited states of  $\text{NO}_2^+$ . In this respect,  $\text{NO}_2$  is representative of many free-radical neutrals that form higher-symmetry closed-shell cations. Weak vibrationless thresholds together with long multi-mode progressions have long been a feature of the conventional photoionization spectra of free radicals [3], and will be an issue in combustion free-radical photoionization experiments planned for the ALS.

### HIGH-RESOLUTION PHOTOIONIZATION SPECTRUM OF $\text{NO}_2$

Our experiments have scanned the threshold photoionization spectrum of  $\text{NO}_2$  from 9.5 to 20 eV (130 to 62 nm) with a resolution of 0.003 nm. We achieved ZEKE photoelectron discrimination by exploiting the time structure of the synchrotron radiation source, which consisted of alternating 544 ns periods of illumination followed by 112 ns dark gaps. During irradiation, the experiment maintained a nominally zero electrostatic field across the ionization region of an electron time-of-flight spectrometer. Accumulated ZEKE threshold photoelectrons were then extracted by a 1 V pulse which was applied to the repeller 20 ns after the beginning of each dark gap. The repetition rate of the experiment was thus 1.52 MHz. Figure 1 shows a complete scan over the region from 9.5 to 20 eV using a counting time of 30 seconds per point.

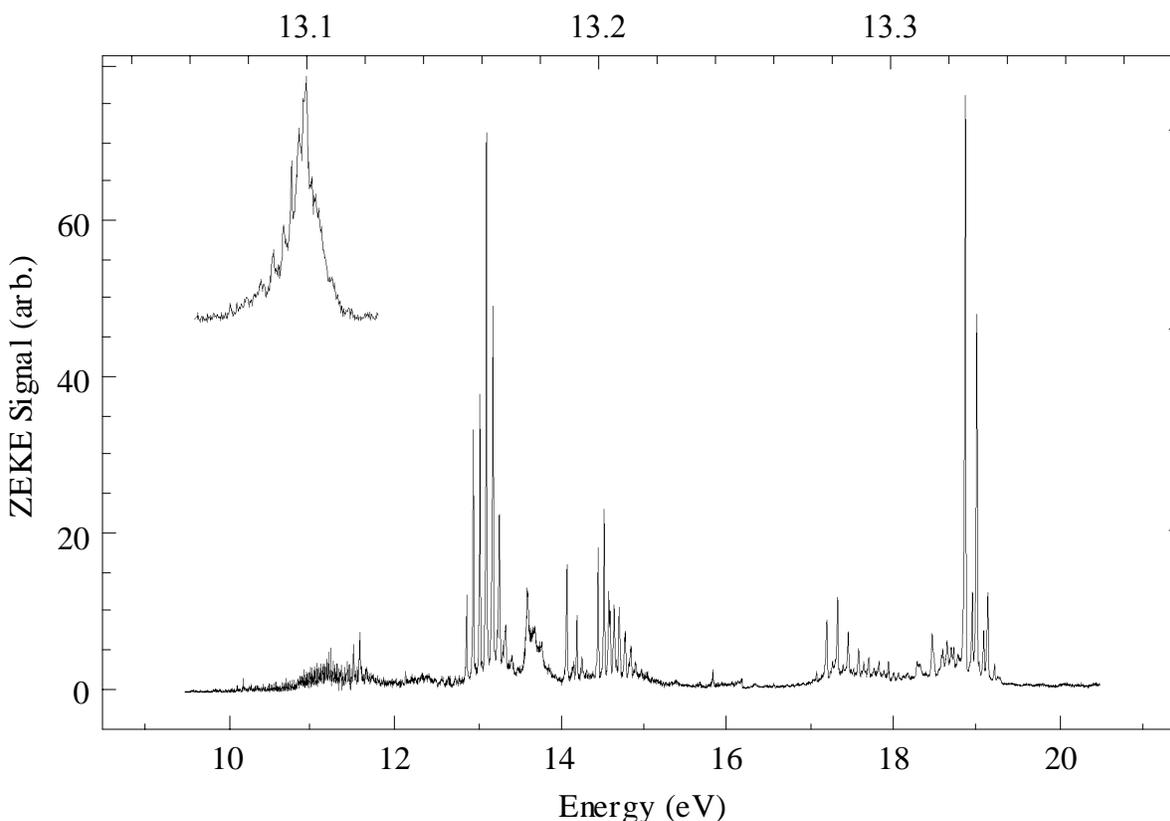


Figure 1. ZEKE threshold photoionization of  $\text{NO}_2$  recorded at the Advanced Light Source.

ZEKE threshold photoelectron discrimination clearly resolves vibrational structure in these many electronically excited states of  $\text{NO}_2^+$ . The inset gives an expanded view of the (030) band of the  $a^3\text{B}_1$  state, which shows that this approach can isolate electronically excited states of polyatomic cations with rotational resolution.

The ZEKE spectrum in the region of the cation ground state exhibits a broad envelope of transitions built on progressions in  $v_2$  arising from bent-to-linear photoionization. Figure 2 shows a detail from the adiabatic threshold to 11 eV (upper spectrum). Weak but evident are some of the same low-frequency bands that we observed in ZEKE spectra scanned in laser-induced transitions from the  $3p\sigma$   $^2\Sigma_u^+$  Rydberg state. With increasing energy, individually assignable bands give way to a complex system of irregular resonances that arise from bend-bend and bend-stretch interactions. The simulation presented in Figure 2 (lower, inverted spectrum) is constructed strictly from our force-field parameterization of the lower energy structure observed in higher-resolution laser experiments described above.

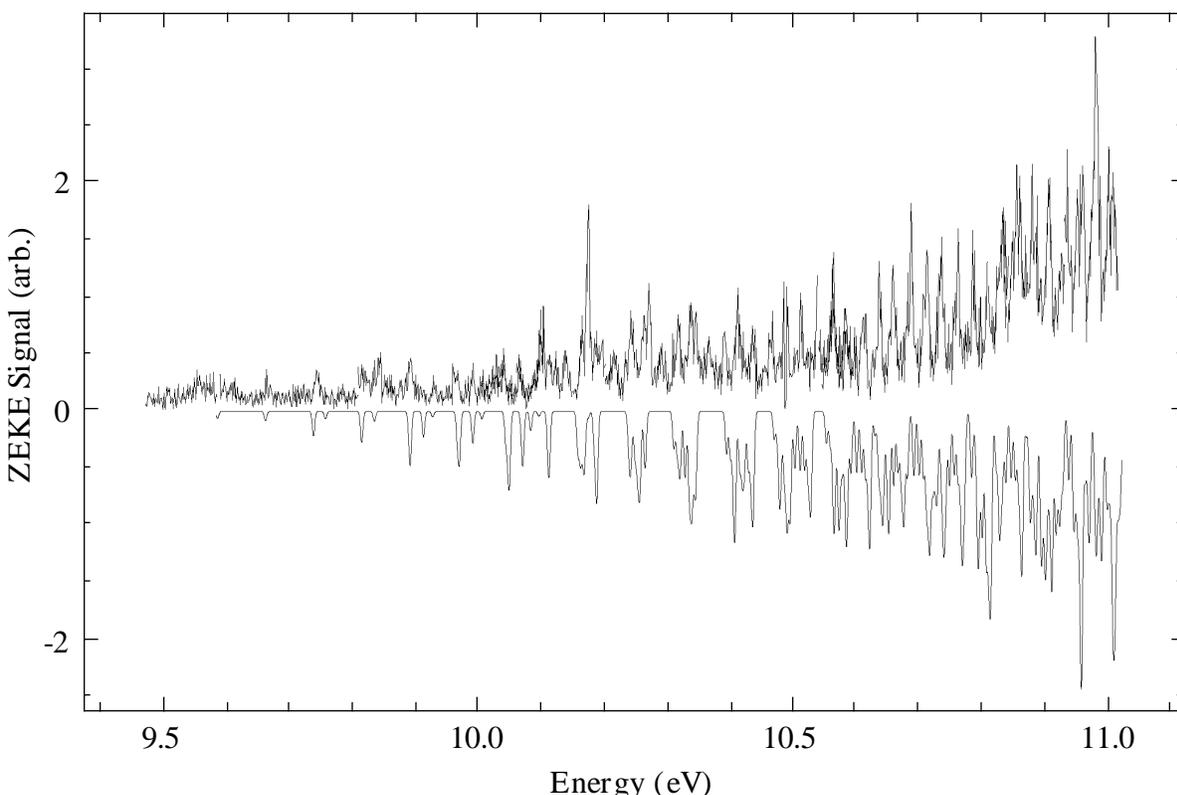


Figure 2. ZEKE threshold photoionization of  $\text{NO}_2$  in the first threshold region. Simulation of cation vibrational structure using spectroscopic parameters derived from our earlier laser photoionization studies.

Further work will refine our higher-order characterization of the  $\text{NO}_2^+$  vibrational potential by improving the experimental spectrum. The use of a supersonic jet in the ALS photoionization apparatus will provide a greater degree of cooling and increase sample density in the interaction region. This will sharpen the threshold photoionization spectrum and improve its signal to noise ratio. We will also complement our ALS data with higher-resolution VUV laser scans over key features using our laboratory ZEKE spectrometer. With better-resolved spectra, we will refine our force field to extend assignments for comparison with variational calculations of vibrational energy levels on ab initio potentials. An important issue will be the vibrational wavefunctions themselves and the detailed redistribution of Franck-Condon intensity that arises from bend-stretch mixing due to off-diagonal and higher-order anharmonicities.

## ACKNOWLEDGMENTS

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