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Spectroscopically resolved competition between dissociation and detachment from nitrobenzene radical anion

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Dedicated to Prof. John R. Eyler on the occasion of his 65th birthday, honoring his contributions in IRMPD ion spectroscopy and mass spectrometry in general.

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ABSTRACT

We report the vibrational spectrum of the gas-phase isolated nitrobenzene radical anion. The spectrum has been acquired by infrared multiple-photon absorption induced dissociation and electron detachment using the FT mass spectrometer coupled to the infrared free-electron laser FELIX. Upon wavelength-dependent multiple-photon absorption of intense IR irradiation, the vibrational spectrum acquired by on-resonance dissociation to NO_2^- was shown to correlate with the more sensitive electron detachment channel which is indirectly observed by using SF_6 as electron scavenger. The spectrum is compared to previous spectroscopic studies and novel DFT calculations. The frequency and intensity changes of the vibrational bands for the radical anion with respect to the neutral are interpreted with the aid of molecular orbital calculations and mode projection analysis. The vibrations of the neutral and the anion are interpreted in terms of the component benzene modes. The anion shows a reversal of the familiar strongly deactivating meta-directing electrophilic aromatic substitution effect of the neutral due to a resonance effect placing electron density at the ortho- and para-positions, resulting in a structure of distonic character. The greater abundance of the electron detachment channel over the NO_2^- loss dissociation channel is interpreted in terms of statistical models of the energy-dependent unimolecular rates. The anion and neutral vibrational frequencies employed in a quasi-equilibrium theory (QET) model of electron detachment compare favorably to previous experimental results of metastable anion autodetachment lifetimes. The ratio of dissociation to detachment is investigated as a function of FEL power and the competition between these channels is in agreement with a statistical model.

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1. Introduction

Both the electron attachment and dissociation properties of nitroaromatic compounds are ultimately responsible for their utility as explosives. One of the initial reaction steps involves electron transfer and the NO_2 loss is the key step. Nitroaromatic compounds are also essential components of chemical synthesis; the simplest example, nitrobenzene, is of unique importance as the primary source for industrial aniline synthesis via a hydrogenation reaction. The nitro group serves as a classic case of a deactivating, meta-directing electrophilic aromatic substitution agent, due to the unimportance of π-resonances donating electron density to the ring in favor of resonances placing electron density on the nitro-substituent. The relative unimportance of the π-resonance between the nitrogen and aromatic ring results in the dominance of inductive effects removing electron density from the ring. The strength of this effect is sufficient to inspire curiosity regarding the influence of electron attachment upon this property.

The electron withdrawing effect of the nitro-moiety is related to the large electron affinity of the neutral and hence overall stability of the radical anion. The electron affinity (EA) of NO_2 is 2.2 eV [1] while that of nitrobenzene is 1.0 eV [2]. However, the stabilization of the excess charge in the anion is also facilitated in large part by the phenyl system. The EA of the phenyl C_6H_5 radical is 1.1 eV [3], as compared to the only barely positive EA of the methyl radical (CH_3) [4]. This results in a large difference between the electron affinities of nitrobenzene and nitromethane (EA = 0.2 eV) [5,6], demonstrating the importance of the aromatic resonance in the nitrobenzene anion. The apparent importance of the phenyl system in stabilizing the excess charge of the nitrobenzene anion again leads to the question of the charge distribution in the anion and the change in bonding properties relative to the neutral. A particularly sensitive probe of these properties is vibrational spectroscopy, as shifts in vibrational band positions and intensities reveal changes in the bonding properties between neutral and charged species, particularly when complemented with computational analysis. The current study addresses the bonding properties of the anion with

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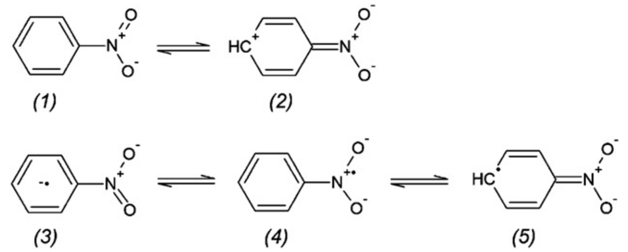

Scheme 1.

the methodology of mass spectrometry based vibrational action spectroscopy in Penning traps as pioneered by the groups of Eyler, Beauchamp, Brauman and others [7].

The bonding properties of the radical anion have been investigated in the condensed phase by electron spin resonance (ESR) of nitrobenzene reduced in solution [8]. These studies suggested an interesting relationship between the neutral and the anion in terms of the resonance interaction of the nitro group with the ring. As shown in Scheme 1, the familiar primary structure of relevance for the nitrobenzene neutral is the pair of structures represented here with a single structure labeled (1) that places partial negative charge on the oxygen atoms to result in partial NO double-bond character and only σ-character for the CN bond. The possible resonance involving π-bond character of the CN bond labeled as (2) results in a large partial positive charge on the ring and single-bond character of the NO bonds, which is at best not strongly favored [9]. As shown by structure (3), a similar partial double NO bonding structure, as favored for the neutral, can be drawn for the radical anion where the excess charge is delocalized around the ring. Although this resonance structure may not be unimportant, the other structures shown as (4) and (5) are likely more relevant. The distonic radical ion structure shown as (5) is in fact best represented as two resonance structures itself, the one shown, and one placing the radical in the ortho-position. This situation is reminiscent of an aromatic electrophilic activation agent, and in fact the ESR studies [8] demonstrated exactly this property; the anion shows significantly more spin density at the para- and ortho-positions than at the meta-position, suggesting a reversal of the strength of the resonance interaction of the nitro group with the aromatic ring. These ESR studies showed that there is a sharing of the radical character between the nitrogen (resonance structure 4) and the ortho- and para-carbons (resonance structure 5), which explains the calculated shortening of the CN bond in the anion [10]. There are numerous other observable properties that can be expected to manifest this change: vibrational band shifts and torsional barriers, in particular. In addition, computed properties such as charge densities and molecular orbitals [10] can shed further insight on the bonding characteristics of the anion.

In addition to the numerous studies of the nitrobenzene radical anion in the condensed phase, the interesting gas-phase electron attachment behavior of nitrobenzene anion is also well characterized. The nitrobenzene molecule is known to attach low-energy electrons into both dipole-bound [2,11] and valence-bound states [2,12], as well as showing multiple resonances from anionic excited states [2,13,14]. Nitrobenzene has a relatively large cross-section for associative free-electron attachment at zero electron energy [12,14] and the metastable parent anion formed shows a significant lifetime towards autodetachment (on the order of tens of μs to ms) [11,12,15]. Both associative and dissociative electron attachment are known to occur, and many examples of the dissociation of nitrobenzene to produce the NO_2^- ion have been observed from relatively low-energy electrons [13,14,16]. While higher energy scattering resonances are implicated in dissociative electron attachment at certain energies, Pelc et al. [14] identified a low-energy dissociative resonance that corresponds to the expected dissociation energy from the electronic ground state. Thus, due to the comparable efficiencies of dissociation and detachment, the ion may be expected to show a competition between these processes upon activation.

The characteristics and stability of the anion have previously been spectroscopically investigated by photoelectron [2], vibrational autodetachment [6,17] and matrix-isolation IR [10] methods. The spectroscopy has established that the nitrobenzene anion undergoes a significant overall red-shift of most vibrational modes, induced by a significant structural change of the anion relative to the neutral [10] that can be related to the anti-bonding properties of the lowest unoccupied molecular orbital (LUMO) of the neutral and highest occupied molecular orbital (HOMO) of the anion. Particularly the N–O bonds as well as the C–N bond are of interest in this respect [10]. These studies are in agreement with the condensed-phase ESR results, namely, the weakening of the bonding in nitrobenzene upon electron attachment is not global, but rather highly localized and results in the strengthening of certain bonds at the expense of others.

The vibrational spectroscopy of negative ions in the condensed phase is common, and matrix-isolation infrared absorption spectroscopy provides a great improvement to solution-phase spectra by reducing the perturbation from the environment. The infrared spectroscopy of gas-phase anions, however, is a developing field for both complexed and isolated species. As discussed in several recent review articles [7,18,19], the vibrational spectroscopy of negative ions is greatly facilitated by infrared action spectroscopies such as vibrational predissociation, vibrational autodetachment, and infrared multiple-photon dissociation and detachment (IRMPD). The particular advantage of IRMPD spectroscopy is that it provides an opportunity for measurement free of intermolecular perturbation in the IR “fingerprint” region even in strongly bound negative ions. Although comparisons of cationic IRMPD spectra to vibrational predissociation spectra and matrix-isolation IR spectra demonstrate the matrix perturbations are typically of small consequence [20], the vibrational spectroscopy of gas-phase anions is relatively less explored, and it is thus essential to consider the effect of the environment. Most gas-phase anionic IRMPD studies to date have focused on the conjugate bases of closed-shell organic [21–28] or inorganic acids [29] (or complexes thereof [30–34]), or transition metal clusters [35,36], but fewer studies [37–39] have examined the spectroscopy of stable radical anions formed via direct electron attachment processes, a class of anions for which numerous vibrational predissociation and matrix-isolation studies have been reported. A recent comparison of matrix-isolation, vibrational predissociation, and IRMPD spectra for the SF_6^- and SF_5^- radical anions [37,40,41] demonstrated rough agreement between the methods, but few bands were available for comparison. A similar situation exists for the C_{60}^- radical anion, also with very few IR-active bands [38,42]. The current study provides an opportunity for direct comparison of a radical anion with a significant number of active vibrational bands to derive a more quantitative measure of agreement.

The use of multiple-photon absorption of negative ions stored in ion traps for action spectroscopy has been reviewed, but few have discussed the relevance of the method for negative ion dynamics [43,44]. IRMPD spectroscopy of negative ions is a multidimensional tool as it inherently contains information about the competition between electron detachment and dissociation. This is analogous to the competition between dissociation and thermionic emission observed in strongly bound neutral molecules such as C_{60} [45]. In this sense it provides a unique opportunity to relate to the previously observed phenomenon of metastable negative ions formed from free-electron attachment [12,46]. IRMPD of a negative ion can be considered as a comparative study to free-electron attachment