



Editor's choice

Rotational auto-detachment of dipole-bound anions

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ABSTRACT

Rotational auto-detachment of acetonitrile, trimethyl-acetonitrile, acetone, and cyclobutanone dipole-bound anions was studied under varying conditions in a Rydberg electron transfer (RET) time-of-flight apparatus. Varying amounts of auto-detachment was observed for anions with similar electron affinity and dipole moment, but different moments of inertia. These results were found to be consistent with predictions based on the calculated rotational spectra for these anions, highlighting the importance of critical binding properties in understanding the stability and lifetime of dipole bound systems.

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1. Introduction

An electron can be bound to any molecule that possesses a sufficiently large dipole moment into what is often called a dipole-bound negative ion state. Numerous authors [1–9] have calculated the minimum dipole moment of 1.625 D for electron binding to a fixed dipole. Below this critical value, no bound states are supported by the electric dipolar field, and for dipole moments above this value an infinite number of bound states exist. However, the critical moment for binding to a 'real' molecule depends upon the dipole length, the moment of inertia, and the rotational quantum state of the finite dipole [10]. These calculations show a low binding energy as a function of the dipole moment for linear molecules until approximately 2 D where the binding energy becomes comparable to the rotational energy of most molecules. This prompted Crawford and Garrett [11] to predict that any polar molecule with a dipole moment above ~ 2 D will form a bound state. Although electron binding to molecules with dipole moments as low as 2 D have not yet been reported, these general predictions have been verified for a large number of polar molecules (see the reviews by Desfrancois et al. [12] and Compton and Hammer [13]). Electron affinities for many of these molecules are reported in these reviews using Rydberg electron transfer (RET), field detachment, and photoelectron spectroscopy methods. In one study, dipole-bound electron affinities for 40 polar molecules have been published and the electron affinities range from ~ 0.5 meV for low (~ 2.5 D) dipole moment molecules to ~ 20 meV for high (~ 4 D) dipole moment molecules

[14]. In these studies it was necessary to employ nozzle-jet expansion of the polar molecules with low dipole moments in order to produce stable anions. From these observations it has been assumed that at room temperature molecules of the weakly polar species are subject to rapid rotational auto-detachment. The stability of these weakly bound, diffuse dipole-bound anions is also sensitive to electric fields and collisions. Suess et al. [15,16] have also shown that dipole-bound anions held in a Penning trap possess relatively short lifetimes (~ 50 – 100 μ s) which was attributed to black-body-induced photo-detachment. A 300 K blackbody spectrum peaks at a photon energy of ~ 120 meV, well above the photo-detachment threshold for all known dipole-bound anions. Calculated lifetimes by Chernov et al. [17] based upon direct photo-detachment are in agreement with these measurements. It is important to note that the stored ions in the experiments by Suess et al. [15,16] were first made from RET with room temperature gas molecules before injection into the Penning ion trap.

For dipole-bound anions, rotational excitation is very important in its effect on the bound state spectrum and on the lifetimes of such systems. When rotational degrees of freedom are included in non-Born–Oppenheimer calculations of model systems [18] and real anions [19–21], the number of excited states of supercritical systems is reduced from an infinite number down to only a few. The rotational spectrum crosses from bound states over to a rich spectrum of rotational resonances of different widths [21,22]. Clary [23] and Simons [24] have considered these effects. Simons made modifications to the original rotationally adiabatic model of Clary to calculate the rotational auto-detachment lifetimes for the CH_2CN^- anion for $J = 31$ – 39 . In the more recent work by Fosseze [21], the use of complex-energy bases provided bound states and rotational-resonance energies and widths for HCN anions. The groups of Brauman [25] and Lineberger [26] have reported very narrow

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resonance features in the photo-detachment thresholds for valence to dipole-bound anion transitions corresponding to rotationally excited shape and Feshbach resonances for many dipole-bound radical anions.

In a recent study, Garrett [27] has extended results for the polar anion problem to include critical binding by polar symmetric top molecules. For the symmetric top, the effects due to rotational degrees of freedom are very different from the earlier results for linear rotors [18–21], indeed a new set of critical moments can be defined for these systems. For symmetric tops possessing non-zero rotations about the axis of symmetry (which contains the direction of the dipolar vector) a finite bound state spectrum transitions into an infinite number of bound states when the dipole moment exceeds newly defined critical values [27]. These new properties are germane to the present study.

In this study we experimentally examine the auto-detachment lifetimes for a series of dipole-bound anions formed by RET to nozzle expanded polar molecules. The molecules studied include symmetric and asymmetric tops that were chosen for their dipole moments, and moments of inertia.

2. Experimental

The apparatus and procedure employed to prepare the dipole-bound anions has been previously described [15–17]. Briefly, Rydberg electron charge exchange (RET) occurs between the dipolar molecule of interest and highly excited Rb atoms. The Rb source consists of a resistively heated alkali oven held at 180 °C producing a steady vapor of atomic Rb. This Rb vapor was then excited to various $ns^2S_{1/2}$ and $nd^2D_{5/2, 3/2}$ states via resonant two-photon excitation. The states were excited using the output of a tunable pulsed dye laser (Quanta Ray) pumped by the second harmonic (532 nm) of the fundamental (1064 nm) of an ND:YAG laser (Continuum Powerlite).

The molecules studied were introduced to the interaction region by an RM Jordan pulsed supersonic valve aligned mutually orthogonal to the beam of excited Rb atoms and the direction of the time-of-flight mass spectrometer. The molecules were seeded in Argon to promote rotational and vibrational cooling to allow for the greater production of the dipole bound states. The Rydberg atom transfers its electron to the polar molecule forming a dipole-bound anion. After an interaction time of ~ 700 ns the anions were extracted with a voltage pulsed to a ~ 1 m long time-of-flight mass spectrometer. The ions, as well as neutrals resulting from all subsequent detachment processes (auto-, collisional- and photo-detachment), were then detected using a z-stack channel plate detector. The z-stack was used to more effectively detect low energy neutral particles.

An important aspect of the time-of-flight setup that allows for the detection of the neutrals is a ~ 10 cm region prior to the detector that focusses and decelerates the ions. The dipole bound anions will become neutralized as they travel down the flight tube as a result of blackbody photo-detachment and rotational auto-detachment. The neutrals that have been produced will then proceed without this deceleration, allowing for a shorter time of flight enabling them to be distinguished from the ion signal. The neutral signals display a tail to high time to a varying degree, indicating detachment in the decelerating region. The overall time-of-flight as well as the separation in time of the neutrals and ions was measured exactly as predicted from modelling by SIMION [28].

Verification of the neutral peaks came from the application of both magnetic and electric fields. A movable permanent magnet (~ 200 G) was placed perpendicular to the path of the ions and neutrals down the flight tube. The ion signal is deflected by this magnetic field and disappears completely while the neutral signal remains unaffected. The magnitude of the neutral signal

Table 1

Relevant experimental [14] and calculated structural properties of the molecules studied.

	Acetonitrile	Trimethyl-acetonitrile	Acetone	Cyclobutanone
EA	19.3 meV	13.2 meV	2.5 meV	1.7 meV
μ	3.92 D	3.95 D	2.88 D	2.89 D
I_{xx}	11.33 a.u.	397.41 a.u.	179.04 a.u.	169.26 a.u.
I_{yy}	198.6 a.u.	658.33 a.u.	211.86 a.u.	374.06 a.u.
I_{zz}	198.6 a.u.	658.33 a.u.	386.59 a.u.	499.64 a.u.

varied dependent upon how far down the flight tube the magnet was placed. The ability to deflect ions in various positions down the flight tube allows an approximate indication of where the auto-detachment was taking place as well as to evaluate the relative contribution of the blackbody photo-detachment. Additionally, electrodes between the flight tube and detector were held at varying voltages having a pronounced effect on the time-of-flight of the ion signal and not the neutral signal. Finally, stable anion signals, such as Cl^- result in no observable neutral signal despite significantly larger anion signal.

Table 1 shows the molecules studied, their calculated moments of inertia, and experimentally determined dipole moments and electron affinities [14]. The dipole moments and electron affinities are important as they are expected to play a role in the blackbody photo-detachment of these anions [1]. The moments of inertia, primarily those orthogonal to the dipole moment, are likewise expected to play an important role in the relative formation initially and later detachment of the present set of anions. The molecules were chosen as pairs with similar dipole moments and electron affinities, differing primarily in moments of inertia. Note that the first pair are symmetric top molecules, the second pair are asymmetric tops. These sets of molecules were chosen specifically to explore the effects of rotational auto-detachment on the formation and survival of dipole bound anions under various experimental conditions.

Production of the neutral signal was highly dependant on experimental conditions, primarily the background pressure inside the interaction region. This background pressure is affected by the amount of gas pulsed in as well as the pumping taking place in the interaction region, thus exact repetition of experimental conditions were quite difficult. This is rather vital as higher pressures in the interaction region caused a greater relative amount of neutral as compared to the ion signal. This is likely caused by rotational excitation caused by collisions with the background gas. Collisional detachment may be present as well, but the neutrals produced in that manner would not have the full acceleration provided by the pulsed voltage and thus would not be observable.

3. Results

In order to consolidate the data and to compensate for experimental variability between tests, comparable pairs of molecules were studied simultaneously. This was possible due to each pair of molecules having similar RET spectra (i.e. signal versus Rydberg level or n^*), due to their similar electron affinities. Due to potentially varied cooling efficiencies and RET cross sections for the molecules, little can be derived from the relative intensities between the ion pairs in the present experiment, thus we focus on the relative ion to neutral signal observed. Figure 1 shows the ion and neutral signals from production of dipole bound acetonitrile and trimethyl-acetonitrile anions for various pressures in the interaction region. The previously mentioned pressure dependence is clearly evident. As the pressure in the interaction region is increased, we see an increase in the amount of neutrals detected with minimal impact on the ion signal. In this case the pressure was varied by limiting the out pumping of the interaction region. A

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