Electron attachment to strongly polar clusters

Formamide molecule and clusters

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Abstract. Electron localization is studied in formamide cluster anions. The isolated formamide molecule has a large dipole moment and its clusters can give birth to multipole-bound anions as well as valence anions. The vertical valence electron affinity of the isolated molecule is determined by electron transmission spectroscopy. The anion formation process is studied as a function of cluster size with Rydberg electron transfer spectroscopy. DFT calculations of the neutral and negatively-charged cluster structures show that the anion excess electron localizes on a single molecule. The adiabatic valence electron affinity of isolated formamide is deduced from the observation of the cluster size threshold for valence attachment.

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1 Introduction

Different low-energy electron attachment processes compete in polar molecular systems. Excess electrons can enter molecular orbitals in conventional (valence) anions or remain located nearly totally outside the molecular frame in multipole-bound anions. Multipole-bound anions can only be created if the dipole and/or quadrupole moments of the parent systems exceed critical values [1,2]. Clusters of molecules with individual dipole moments below the critical value ca. 2.5 D can also bind excess electrons either internally as in solvated electrons or in diffuse orbitals as surface states or multipole-bound states [3–5]. When the valence electron affinity of the constituting polar molecule is negative, transient valence anion formation appears as a resonance in the free-electron scattering cross-section of the neutral monomer [6]. When polar molecules are embedded in a cluster, the total multipole (dipole and/or quadrupole) moments of the most stable configurations can exceed or be lower than the critical values [7] and excess electrons can be bound or not, then leading to magic numbers in the anion mass-spectra [8,9]. When the cluster size further increases, solvation effects become more and more important and valence electron binding enters into competition with electron multipole binding. Above a threshold size value \( N_{th} \), the cluster valence electron affinity becomes positive and a smooth anion mass distribution is observed.

In the most widely studied case of anion water clusters, the mass-spectra exhibit magic numbers \( N = 2, 6, 7 \) and become smooth above \( N_{th} = 10 \) [10–12]. In ammonia clusters, there are no magic numbers and a smooth mass-spectrum is observed for cluster sizes above \( N_{th} = 33 \) [10,12]. Both water and ammonia have a dipole moment much smaller than the critical value for electron binding. The theoretical interpretation of the observed mass-spectra is then very difficult and the structure of water anions is still the subject of elaborated experimental [5,9] and theoretical studies [2,8].

In the present work, our attention is focused on valence electron attachment to the isolated formamide molecule which possesses a dipole moment of 3.72 D, much larger than the critical value, and to its homogeneous clusters. In gas-phase collisions, the isolated formamide molecule can temporarily attach a free electron of appropriate energy and angular momentum into a vacant MO, the process being referred to as a shape resonance [13]. Electron transmission spectroscopy (ETS) [14] is one of the most suitable means for detecting the formation of such short-lived anions. Because electron attachment is rapid with respect to nuclear motion, the temporary anion is formed in the equilibrium geometry of the neutral molecule. The impact electron energy at which electron attachment occurs is properly denoted as vertical attachment energy (VAE)
and is the negative of the vertical electron affinity. The ETS spectrum of isolated formamide is here reported for the first time.

We also here consider electron binding to formamide clusters. The electron source is then a laser-excited Rydberg atom source [12, 15]. We have already shown that the magic island \((N = 1, 2\) and 3), which appears in the formamide anion mass-spectrum observed in collisions between Rydberg atoms and neutral formamide clusters, can be interpreted in terms of creation of multipole-bound anions [16]. This interpretation has been confirmed by means of infrared spectroscopy which provides information about the geometrical structures of the neutral precursor of the formed anion [17].

Since formamide is an important model compound for hydrogen bonding and peptide linkage, the structures of the neutral parent clusters have been widely theoretically studied but, to our knowledge, the only studied ionized formamide clusters are either the protonated clusters up to \(N = 3\) [18] or the multipole-bound anions up to \(N = 3\) [16]. The experimental results of a rather similar study of electron attachment to \(N\)-monosubstituted amide clusters up to large values \((N = 23)\) have been published [19] and will be compared to the present results. From the experimental observation of the size threshold for valence electron attachment and calculations of binding energies of both neutral and anion clusters, we here deduce the valence adiabatic electron affinity of formamide which we compare to theoretical predictions.

2 Experimental procedure

2.1 Electron transmission spectrum

The electron transmission apparatus presently used is in the format devised by Sanche and Schulz [14] and has been previously described [20]. To enhance the visibility of the sharp resonance structures, the impact energy of the electron beam is modulated with a small ac voltage, and the derivative of the electron current transmitted through the gas sample is measured directly by a synchronous lock-in amplifier. Each resonance is characterized by a minimum and a maximum in the derivative signal. The energy of the midpoint between these features is assigned to the most probable VAE. The present spectrum was obtained by using the apparatus in the “high-rejection” mode [21] and is, therefore, related to the nearly total scattering cross-section. The electron beam resolution was about 50 meV (fwhm). The energy scale was calibrated with reference to the \((1s^12s^2)^2S\) anion state of He which energy is 19.37 eV at its minimum in the derivatised signal. The estimated accuracy is \(\pm 0.05\) eV.

The results of our ET measurements in \(\text{H}_2\text{NCHO}\) are shown in Figure 1, where the derivative of the transmitted current is plotted as a function of the electron impact energy over the range from 0.5 to 6 eV. The ET spectrum displays a single distinct resonance, located at 2.05 eV (fwhm = 0.82 eV). Such an intense feature is expected to be associated with electron capture into the empty \(\pi^*\text{CO}\) MO (Fig. 2a). A corresponding resonance has been observed in the ET spectra of formaldehyde [22] (VAE = 0.86 eV), acetone [23] (VAE = 1.31 eV) and cyclic monoketones [23, 24] (VAE = 1.00, 1.15 and 1.30 eV for the four-, five- and six-membered cycles, respectively). The destabilisation (about 1 eV) caused by the amino substituent on the \(\pi^*\text{CO}\) anion state is in line with previous ET data, and has been ascribed to charge-transfer interaction with the adjacent nitrogen lone pair [23].

![Fig. 1. Derivative of the electron current transmitted through formamide vapour, as a function of the electron energy. The vertical line locates the VAE.](image)

![Fig. 2. Excess electron orbital: (a) in the formamide monomer valence anion; (b) in the formamide monomer dipole-bound anion.](image)