Long-Range Electron Binding to Quadrupolar Molecules

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An excess electron can be bound to a molecule in a very diffuse orbital as a result of the long-range contributions of the molecular electrostatic field. Following a systematic search, we report experimental evidence that quadrupole binding occurs for the *trans*-succinonitrile molecule (EA $= 20 \pm 2$ meV), while the *gauche*-succinonitrile conformer supports a dipole-bound anion state (EA $= 108 \pm 10$ meV). Theoretical calculations at the DFT/B3LYP level support these interpretations and give electron affinities of 20 and 138 meV, respectively.

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An excess electron can be trapped in the molecular potential well essentially created by the long-range attractive fields plus a short-range repulsive core potential. In the case of the dipolar potential, a minimum dipole moment of about 2.5 D is required for the formation of stable dipole-bound anions. Electron affinities (EAs) ranging from a few tenths to a few tens of meV have been predicted [1] and measured [2–4]. The average distance between such a loosely bound electron and the polar molecule is then as large as several tens of Å and the excess electron mainly experiences the molecular asymptotic dipole field. When the dipole moment becomes too large, e.g., in NaCl⁻, the excess electron orbital is localized close to the positive end (e.g., Na⁺) and is then more characteristic for a conventional valence anion state [5].

Herein we reexamine the problem of the extension of dipole-bound to quadrupole-bound anions. The possibility that an electron might be bound to a molecule as a result of its quadrupole moment was first considered theoretically by Jordan and Liebman [6]. Several theoretical [5,7] and experimental [8,9] studies with conflicting results have since been devoted to this problem. On the experimental side, there has been no firm evidence for the existence of weakly bound anions due to the quadrupolar interactions alone. Experimental data, from Rydberg electron transfer to the formamide dimer [9] and photoelectron spectroscopy of MgO cluster anions [8], have been interpreted in terms of quadrupole-bound anions. However, it can be argued that these interpretations might not be valid due to the lack of theoretical support in the formamide case and to rather well-localized orbitals, close to Mg atoms, in the case of MgO clusters, with rather large EA values (0.5–1 eV). In this paper we present the first solid evidence for very weak electron binding to a molecular quadrupole in the case of *trans*-succinonitrile

(NC-CH₂-CH₂-CN). This conformer has a zero dipole moment and rather large quadrupole moments resulting from the two opposite C-N dipoles, separated by about 5 Å. In contrast to the formamide dimer, their positive ends point inside the molecular frame, in a region where the excess electron cannot be accommodated due to the repulsion with the closed-shell molecular orbitals. In that case, we have to consider the presence of a quadrupolar potential plus a polarization potential as responsible for the long-range electron binding [10,11].

A nearly universal means for the preparation of weakly bound anions is the Rydberg electron transfer (RET) technique. It provides a signature of the nature of the produced anions since Rydberg level *n* dependencies for the formation of either atomic [12] or dipole-bound [3,13] anions are always sharply peaked, in contrast to the case of most valence anions. This RET diagnosis can be further confirmed by field-detachment measurements [14]. Using these techniques, we conducted a systematic search for very weakly bound anions which can be ascribed to quadrupole-bound anions. The presence of two identical polar chemical groups in a head-to-tail configuration was an obvious choice. We have measured *n* dependencies of anion creation rates for several molecules substituted by CN, CO, or NO₂ groups and dimers. RET data for these systems either exhibit only smooth valence anion behavior or mixed smooth and peaked behavior, with no observable electric field detachment for fields up to 30 kV/cm. In those cases either quadrupole anion states are too loosely bound to be observed or do not exist (1,4-cyclohexanedione, acetonitrile dimer) or they are too strongly coupled to valence states (1,4-dicyanobenzene, 1,4-dinitrobenzene, fumaronitrile) which preclude their characterization. We here report on the succinonitrile (SN) molecule which exists in both a *trans*- and a *gauche*-conformation and displays all of the properties of

very weakly bound anions characteristic of dipole and quadrupole electron binding.

RET studies were made at Université Paris-Nord (UPN) [10] and at the University of Tennessee (UT) [13]. A neutral molecular beam is created by seeding helium with succinonitrile followed by expansion through a pulsed valve. This rovibrationally cooled molecular beam crosses downstream a beam of laser-excited Rydberg atoms, $Xe(nf)$ ($n^* \sim n$) at UPN or $Rb(nd)$ ($n^* = n - 1.35$) at UT. Anions are created by charge exchange between the molecular beam and the Rydberg atomic beam and they are mass analyzed in a time-of-flight mass spectrometer. Electric field-detachment measurements at UPN are performed by means of a set of three planar grids perpendicular to the anion path [14]. In the anion photoelectron spectroscopic studies performed at Johns Hopkins University (JHU), the succinonitrile anions are generated in a microplasma, mass selected, and then photodetached [2]. The resulting electrons are then energy analyzed with a resolution of about 20 meV.

Let us first consider the predictions that can be inferred from the structure of the neutral parents. The succinonitrile molecule possesses a remarkable property which is the presence of two nearly energetically equivalent conformations (see Table I): a *trans* conformation with a null dipole moment and large quadrupole moments and a *gauche* conformation with a large dipole moment $\mu_g \approx$ 5.7 D and relatively small quadrupole moments [16,17]. Present *ab initio* calculations, at the MP2/aug-cc-pVDZ level (with zero point energy corrections), give an energy difference between the *trans* and the *gauche* conformers of 34 meV. Assuming an internal rovibrational temperature lower than the heating temperature, the relative population of the *gauche* conformer can be estimated to be lower than 26%, most of the molecules being in the *trans* conformation. In the absence of any available experimental value for the quadrupole moments, our calculations provide us the traceless values of $Q_{xx} = +21.6$ a.u., $Q_{yy} = +20.7$ a.u., and $Q_{zz} = -42.3$ a.u. for the *trans* conformer. This corresponds to a charge distribution very close to the cylindrical symmetry with $Q = -42$ a.u. We can thus anticipate the existence of two different anion states corresponding to electron binding to molecules in the *trans*(quadrupole-bound) and *gauche* (dipole-bound) conformations.

The n dependencies of the measured SN^- anion formation rates in RET collisions are displayed in Fig. 1. The main characteristic of this curve is the sharply peaked feature around $n = 12$. In studies performed at UT, for which the Rydberg excitation scheme leads to a higher sensitivity, there is also an additional very small, but reproducible, peak at low n values, around $n = 6–7$. From the peak values of the RET curve, and with the help of a semiempirical law [18], EA = 23 eV/$n^{2.8}$, we derive the EA values of 115 meV ($n = 6.65$) and 22 meV ($n = 12$), for the excess electron binding energies. Fitting the experimental curve with a simple curve-crossing model for RET [18] leads exactly to the same values. The bound state at 22 meV is also independently confirmed by a field-detachment experiment for anions, obtained in RET collisions with $Xe(12f)$ Rydberg atoms. The corresponding detaching field values, in the vicinity of 12 kV/cm, are also characteristic of the creation of anions with excess electrons in diffuse orbitals and provide an EA value of 18 meV [18].

Despite this experimental evidence of the formation of weakly bound anions in RET to SN, the existence of several neutral conformations raises the question of the nature of the excess electron binding. The main peak of the RET curve is similar to those expected for dipole-bound anions in which the parent molecules possess dipole moments between 3 and 4 D [3,13]. However, SN does not possess such a dipole moment: it is 0 for the *trans* conformer and 5.7 D for the *gauche* conformer. This provides the first indication that the main peak cannot correspond to dipole-bound anion formation. On the other hand, the small peak at low n is likely to correspond to dipole-bound *gauche* anion formation, as also strongly suggested from photoelectron spectroscopy data obtained at JHU which give an EA of 108 ± 10 meV for SN anions (Fig. 2). It is thus likely that only the dipole-bound anions, corresponding to the high-dipole *gauche* conformation and to the most stable anion species, are being observed with this technique. The EA value measured by photodetachment is indeed in very good agreement with the low n feature of the RET curve and it fits well with a binding energy of an excess electron bound to a molecular dipole of about 6 D. These data provide strong evidence for our interpretation that the observed weakly bound anions, in the main peak of the

TABLE I.   Calculated total energies E for the neutral and anion conformers of succinonitrile (SN) as obtained by full optimization at the DFT/B3LYP level, using homemade optimized basis sets [15]. The corresponding calculated and experimental EAs and the calculated dipole and quadrupole moment values of the neutrals are also given.

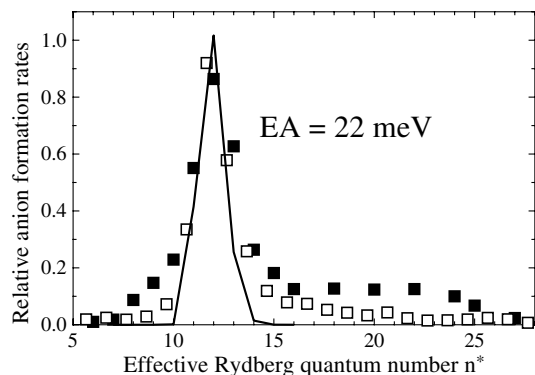| SN *conformer*	E neutral (a.u.)	E anion (a.u.)	EA calc. (meV)	EA exp. (meV)	μ_Z (D)	Q_{XX} (a.u.)	Q_{YY} (a.u.)	Q_{ZZ} (a.u.)
SN *trans*	264.326 996	264.327 739	20	20 ± 2	0.00	−44	+23	+21
SN *gauche*	264.325 188	264.330 246	138	108 ± 10	5.73	−21	+14	+7

FIG. 1.   Rydberg electron transfer (RET) curves for succino-nitrile anion production as a function of the effective Rydberg quantum number n^* involved in the electron transfer collisions with either $Xe(nf)$ states (solid squares) or $Rb(nd)$ states (open squares). The full line is a fit to these experimental points, using a curve-crossing model [18] with the only parameter being the excess electron binding energy EA.

RET data, can be attributed only to the null dipole conformation of succinonitrile. Thus, the present observations constitute the first clear experimental demonstration of the existence of anions with excess electrons in very diffuse orbitals created from a closed-shell molecule with a null dipole and large quadrupole moments.

In order to test this interpretation, we have performed quantum chemistry and semiempirical calculations on weakly bound anions of SN. First, density functional theory (DFT/B3LYP) calculations have been performed on neutral and anion conformers, with optimized appropriate diffuse basis sets that give accurate dipole-bound EA values for water dimer [15] and acetonitrile anions [10,19]. The results for SN are given in Table I and fit very well the present experimental data: we obtain EA = 20 meV for the *trans* conformer and EA = 138 meV
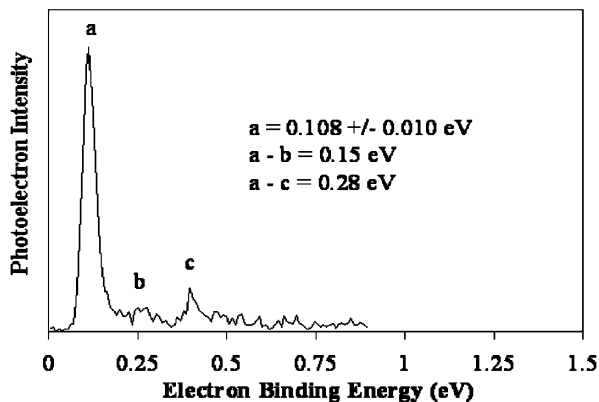

FIG. 2.   Anion photoelectron spectrum for succinonitrile anions produced in a supersonic ion beam source. The main peak *a* corresponds to the transition between the anion and neutral ground states, from which EA = 108 ± 10 meV is determined, while peaks *b* and *c* correspond to transitions towards excited rovibrational levels of the neutral.

for the *gauche* conformer. For the *trans* and the *gauche* anion conformers, the corresponding diffuse excess electron wave functions [anion highest occupied molecular orbital (HOMO)] are displayed in Fig. 3. It is clearly seen that the *gauche* conformer corresponds to a dipole-bound anion in which the excess electron is mainly located on the positive side of the total charge distribution. On the contrary, in the *trans* anion conformer, the excess electron orbital looks like a torus about the z axis of the two opposite CN dipoles. The weakly bound electron is thus mainly located close to the plane perpendicular to this axis, which is indeed the plane of the more attractive quadrupolar potential, due to the negative quadrupole moment value.

The potential energy surfaces of the neutral and the anion species along the coordinate that connect the *trans* and the *gauche* conformations are represented in Fig. 4. It is clearly seen that, contrary to the neutral case, the *gauche* dipole-bound conformer is the most stable form of the anion. It is well separated from the *trans* quadrupole-bound conformer by an energy barrier (>100 meV) at least as high as in the neutral, which prevents interconversion.

A key question is whether electron binding occurs as a result of the overall quadrupole potential or the local dipole potentials. In the case of SN, i.e., for negative quadrupole moments, the terminal nitrogen atoms possess negative partial charges while the attached carbon atoms are more or less positively charged. An excess electron bound by one local CN dipole would then have to be localized close to the corresponding carbon atom, where valence interactions are at least as important as electrostatic ones. However, the weak binding energies measured here along with the above calculations show that the excess electron occupies a diffuse orbital, close to the plane perpendicular to the two opposite dipoles as displayed in Fig. 3, in which it is mainly supported by the long-range part of the quadrupolar interaction.

From the present positive result regarding the formation of stable but weakly bound anions of *trans* succinonitrile ($Q \approx -42$ a.u.) and our negative results for
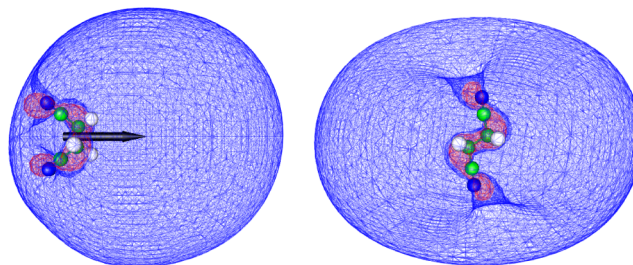

FIG. 3 (color online).   Highest occupied molecular orbital (HOMO) for the *trans* (left) and the *gauche* (right) conformers of succinonitrile anions, in 3D perspective view, using the gOpenMol visualization software [20]. Both plots correspond to the same isocontour value of 0.003 a.u.
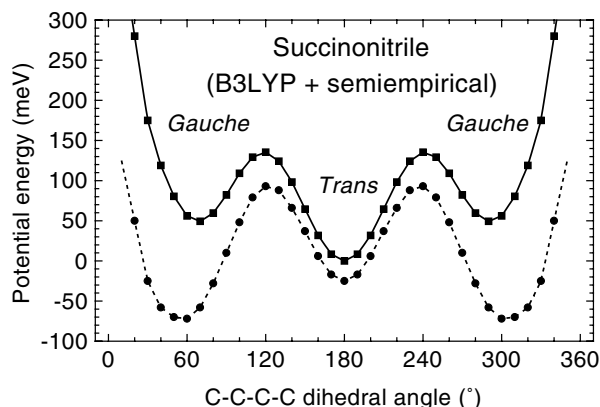
FIG. 4. Potential energy surfaces for neutral and anion succinonitrile along the dihedral angle connecting the *trans* and the *gauche* conformers. Neutral points (squares) have been directly obtained from DFT/B3LYP calculations while anion points (circles) have been calculated from the neutral electrostatic parameters and a semiempirical model [11] of multipole-bound anions. The order of stability between *trans* and *gauche* conformers is reversed in the neutral and the anion but there is still a rather high-energy barrier that prevents interconversion.

1,4-cyclohexanedione ($Q \approx -37$ a.u.), we provide a rough estimate of the empirical critical negative quadrupole moment value, $Q_{min} \approx -40$ a.u., required to bind an excess electron. This value is much higher than the previously reported value (-5.2 a.u. [21]) but it is very much in line with the values derived for positive quadrupole moments ($+41$ a.u. [21]) and from semiempirical electrostatic model calculations (-41 a.u. [11]).

In summary, we present the first conclusive evidence for the existence of quadrupole-bound negative ions and empirically derive a minimum value for the quadrupole moment required to form a stable anion. The succinonitrile molecule is particularly interesting because it can give birth to both dipole-bound and quadrupole-bound anions.

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