



ELSEVIER

International Journal of Mass Spectrometry 205 (2001) 7–16



Empty level structure and dissociative electron attachment in gas-phase nitro derivatives

Alberto Modelli^{a,*} and Marco Venuti^a

^a*Dipartimento di Chimica "G. Ciamician", Università di Bologna, Bologna, Italy*

Manuscript received December 13, 1999; revised manuscript received March 12, 2000; accepted March 13, 2000

Abstract

The gas-phase empty level structures of nitromethane, nitrobenzene, 2-nitroanisole and 2-nitrophenol are studied by means of electron transmission spectroscopy (ETS), dissociative electron attachment spectroscopy (DAS) and *ab initio* calculations, in the 0–6 eV energy range. Both the ETS and theoretical results indicate that the vertical electron affinity is positive in nitrobenzene, but negative in nitromethane. Consistently, the DA spectra of the nitrobenzenes display an intense molecular anion current at zero energy, while in nitromethane only the NO_2^- fragment (peaking at 0.6 eV) is observed. The most abundant anion is NO_2^- , also in the DA spectra of the nitrobenzenes, although in 2-nitrophenol the loss of the hydroxy radical from the molecular anion gives rise to a signal of the same intensity. Interestingly, the ET spectra of nitrobenzene and 2-nitrophenol display one and two narrow features, respectively, below 4 eV not associated with simple electron capture into π^* orbitals. These signals are ascribed to core-excited resonances lying at exceptionally low energy. Comparison between the anion current measured with a quadrupole mass filter and that measured at the collision chamber suggests that the occurrence of intramolecular hydrogen bonding in 2-nitrophenol increases the lifetime of the molecular anion formed at zero energy. (Int J Mass Spectrom 205 (2001) 7–16) © 2001 Elsevier Science B.V.

Keywords: Electron transmission; Empty level; Dissociative electron attachment; Nitro derivatives

1. Introduction

Electron transmission spectroscopy (ETS) [1] is one of the most suitable means for measuring the energies (attachment energies, AEs) of electron attachment to gas-phase samples, that is, the negative of the vertical electron affinity (EA) values. This technique takes advantage of the sharp variations in the total electron-molecule scattering cross section caused by resonance processes, namely, temporary capture of

electrons with appropriate energy and angular momentum into empty molecular orbitals (MOs) [2]. The most severe limit of the technique is that stable anion states cannot be detected. Additional information can be supplied by dissociative electron attachment spectroscopy (DAS), which measures the yield of long-lived negative ions, as a function of the impact electron energy. When suitable energetic and kinetic conditions occur, the temporary molecular anions formed by resonance can follow a dissociative decay channel before the extra electron is re-emitted. The lifetime of the negative fragments produced is usually sufficiently long to allow detection by means of a mass filter.

* Corresponding author. E-mail: modelli@ciam.unibo.it

Dedicated to Professor Aleksandar Stamatovic on the occasion of his 60th birthday.

Owing to the strong electron-withdrawing inductive effect and to the low energy of the lowest unoccupied (π^*) orbital of the NO_2 functional group, nitro derivatives possess very pronounced electron-acceptor properties. From the reactivity point of view, therefore, the knowledge of their empty level structure is even more important than that of the filled counterpart. While photoelectron spectroscopy and theoretical studies have provided detailed information on the energies and ordering of the filled orbitals in this class of compounds for more than two decades (see, for instance, Refs. [3] and [4]), to the authors' knowledge, the ETS literature is curiously limited to a single work on the reactivity of a large conjugated π -system [5]. DAS information also is very scarce, the negative ion yields measured, as a function of the incident electron energy, in nitrobenzene [6] and measurements of the lifetime of the parent anion formed at zero energy in nitrobenzene derivatives [7–9] being the only available data.

In this paper, nitromethane, nitrobenzene, 2-nitroanisole and 2-nitrophenol are analysed by means of ET and DA spectroscopies and of *ab initio* calculations. The two *ortho*-substituted nitrobenzenes were chosen because of the occurrence of strong hydrogen bonding in 2-nitrophenol [10], but not in 2-nitroanisole. The authors have recently observed that in 2-hydroxybenzaldehyde [11], hydrogen bonding causes an energy stabilisation of the anion states with carbonyl character and increases the lifetime of the molecular anions formed at zero electron impact energy.

A theoretical approach adequate for describing the energetics of temporary electron capture involves difficulties not encountered for the cation states. In principle, the most correct approach is the calculation of the total electron scattering cross section with the use of continuum functions, although evaluation of the electron-molecule interactions is not easy [12]. In the Koopmans' theorem (KT) approximation [13], the negatives of the energies of the filled and empty orbitals equal the ionisation energies and the EAs, respectively. This approximation neglects correlation and relaxation effects, which tend to cancel out when ionisation energies, but not EAs, are evaluated. For

this reason, KT predictions generally underestimate EA values by some eV. The lowest unoccupied molecular orbital (LUMO) eigenvalues determined with Hartree-Fock (HF) 6–31G* calculations, however, were found [14] to correctly parallel the experimental AE trends in homologous compounds, whereas inclusion of diffuse functions (6–31+G* basis set) led to a complete breakdown in the eigenvalues/AEs correlation [14,15]. The use of a finite basis set formed with Gaussian functions, owing to their radial rigidity and the exponential decay, accounts in some way for the confinement of the extra electron to the molecule during a resonance process. As the basis set is enlarged with diffuse functions the empty orbitals are prone to approximate low-energy continuum functions, so that more complex stabilisation procedures are needed in order to distinguish the virtual orbitals associated with temporary anion formation [16,17]. In line with Ref. [14], the authors have recently found that the HF/6–31G** eigenvalues satisfactorily parallel the experimental π^* AE trends in series of acetone oximes [18], substituted diimines [19] and benzaldehydes [11]. Here, they verify if this simple approach is able to reproduce the energy trends of the π^* resonances also in the present nitro compounds. More sophisticated methods, which account for correlation using the coupled cluster theory [20] or the quadratic CI approach [21], are employed for evaluating the absolute values of the first vertical EA of nitromethane and nitrobenzene.

2. Experimental and Calculations

2.1 ET and DA spectra

The electron transmission apparatus is in the format devised by Sanche and Schulz [22] and has been previously described [23]. 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. The present spectra have been obtained by using the apparatus in

the “high-rejection” mode [24] and are, therefore, related to the nearly total scattering cross section. The electron beam resolution, obtained with a trochoidal monochromator similar to that described by Stamatovic and Schulz [25], was about 50 meV (FWHM). The energy scales were calibrated with reference to the $(1s^12s^2)^2S$ anion state of He. The estimated accuracy is ± 0.05 or ± 0.1 eV, depending on the number of decimal digits reported.

The collision chamber of the ETS apparatus has been modified [26] in order to allow for ion extraction at 90° with respect to the electron beam direction. Ions are then accelerated and focused toward the entrance of a quadrupole mass filter. Alternatively, the total anion current can be collected and measured (with a Keithley 485 picoammeter) at the walls of the collision chamber (about 0.8 cm from the electron beam). The DAS data reported here were obtained with an electron beam current about three times as large as that used for the ET experiment. The energy spread of the electron beam increased to about 140 meV, as evaluated from the width of the SF_6^- signal at zero energy.

2.2 Computational details

The calculations on the neutral and anion states were performed with the Gaussian 98 set of programs [27]. Geometry optimisations on the neutral molecules were performed using the second order many-body perturbation theory (MP2) and the 6–31G** basis set [28]. The obtained parameters are in very good agreement with those previously reported for nitromethane [29], nitrobenzene and 2-nitrophenol [10].

The virtual orbital energies of the neutral molecules were evaluated using the 6–31G* and the Dunning/Huzinaga valence double-zeta D95V* (C,O,N: 9s,5p,1d/4s,2p,1d; H: 4s/2s) [30] basis sets. The latter should be more suitable for describing the diffuseness in space of the virtual orbitals.

Post HF methods were used to calculate the first vertical EA value of nitromethane and nitrobenzene. Since second and fourth order many-body perturbation theory (MBPT) seems to be unreliable for pre-

dicting the EA of nitromethane [31], infinite order coupled-cluster expansions were employed, that is, coupled-cluster with all single and double substitutions (CCSD) [32] and quadratic configuration interaction with perturbative inclusion of triple substitutions [QCISD(T)] [21]. To improve the description of the diffuse anion states, the D95V+* basis set was used (with exponents 0.0438, 0.0639 and 0.0845 for the diffuse functions of the C, N and O atoms, respectively). Diffuse functions with lower exponents were not included to avoid the description of low energy dipole bound anions, as described in Ref. [29]. The perturbative expansion of triple substitutions was found to converge much more slowly for the anions than for the corresponding neutral molecules, especially for nitromethane. Thus, the EA values calculated with single and double substitutions only were estimated to be more reliable.

The ground state geometry of the nitromethane anion, required for the evaluation of the adiabatic EA, was obtained with a DFT optimization using a B3LYP hamiltonian and the same basis (D95V+*) used in the post HF calculations. The computed parameters are in close agreement with those reported in Ref. [29].

3. Results and Discussion

3.1 Empty level structures

The ET spectra of the examined nitro compounds are displayed in Fig. 1, and the measured AE values are given in Table 1. These data are reported in a schematic form in the correlation diagram of Fig. 2, together with the outermost ionisation energy values. The three orbital/four electron π system of the NO_2 group possesses only one empty π^* orbital, antibonding and of b_1 symmetry. For sake of clarity, in Fig. 2 the notation of the C_{2v} point group is adopted also for the CH_3NO_2 molecule, although its symmetry is only C_s .

The ET spectrum of nitromethane exhibits an intense and sharp feature ($AE \leq 0.45$ eV) superimposed to the high-energy wing of the electron beam signal. Its invariableness in energy with respect to the

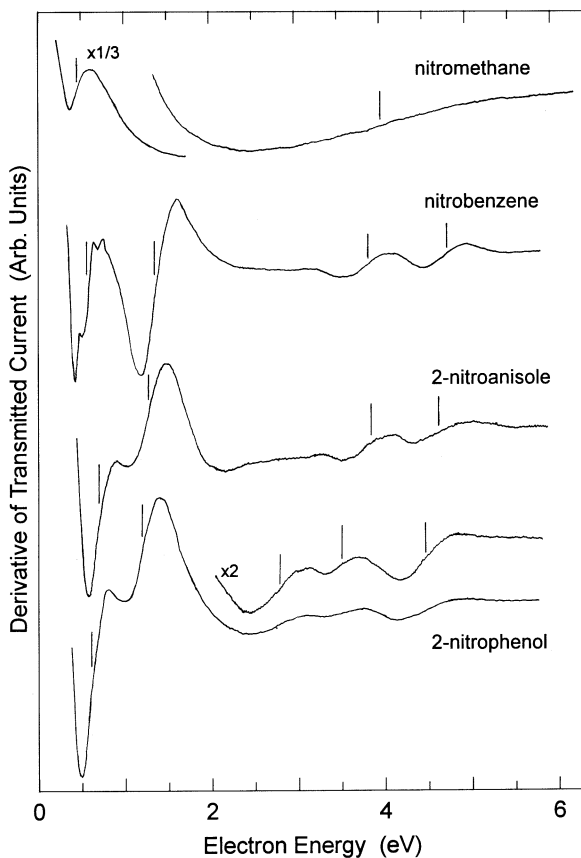


Fig. 1. Derivative of the electron current transmitted through nitromethane, nitrobenzene, 2-nitroanisole and 2-nitrophenol, as a function of the incident electron energy. Vertical lines locate most probable AEs.

retarding potential seems to exclude the occurrence of an instrumental artifact [24]. This structure should thus be associated with electron capture into the π^* LUMO, indicating that the first anion state is unstable with respect to electron detachment. According to measurements of electron-transfer equilibrium constants [33], nitromethane has a positive EA of 0.49 eV. In a more recent negative ion photoelectron spectroscopy study [34], the adiabatic EA value was found to be 0.26 eV, that is, the ground anion state at its equilibrium geometry is 0.26 eV more stable than the ground neutral state at its equilibrium geometry. The instability of the first anion state observed in the ET spectrum is not in contrast with these data, because the anions observed in ETS are formed at the

geometry of the neutral molecule through a vertical transition. In agreement, a theoretical study [29] at the coupled-cluster CCSD(T) and HF/DFT levels of theory predicted a slightly positive (0.11 and 0.22 eV, respectively) adiabatic EA, but a negative vertical EA (although numerical values for the latter were not reported). In the 0.5–6 eV energy range, the ET spectrum of nitromethane shows only a broad and weak signal centered at 4.0 eV; as usually found in second-row compounds [35], narrow σ^* resonances are not present.

Nitrobenzene (C_{2v} point group) has four empty π^* orbitals. The LUMO is expected to possess mainly π^* NO_2 character but to be strongly mixed (and therefore stabilised) with the component of b_1 symmetry of the degenerate benzene π^* (e_{2u}) MO. In agreement, according to electron-transfer equilibrium measurements [33] and to more recent measurements of the equilibrium constant for thermal electron attachment as a function of temperature [36], the (presumably adiabatic) EA of nitrobenzene is 1.0 eV.

In order to support the assignment of the nitromethane ET spectrum and to evaluate the first vertical EA value of nitrobenzene, we performed coupled-cluster and quadratic CI calculations with single and double substitutions, similar to those [29] employed for reproducing the adiabatic EA of nitromethane. Because of the larger size of nitrobenzene, a less extended basis set (D95V+*) was used for both molecules. To verify the reliability of the results, the adiabatic EA of nitromethane was also calculated. The two sets of values (reported in Table 2) supplied by the CCSD and QCISD methods are very close to each other. The positive adiabatic EA calculated for nitromethane is only slightly smaller than that given by the above cited previous calculations and 0.2 eV lower than the experimental value (0.26 eV [34]). The vertical EA of nitromethane is predicted to be -0.5 eV, in nice agreement with the AE of 0.45 eV measured in the ET spectrum, while a positive vertical EA of ~ 0.35 eV is calculated for nitrobenzene.

Based on these considerations, the first anion state of nitrobenzene is stable and thus not observed in ETS. The first resonance displayed by the ET spec-

Table 1

Resonance energies and widths (FWHM) measured in the ET spectra, and peak energies and relative intensities (as evaluated from the heights of the signals) measured in the total and in the mass-selected anion currents

| | ETS | | Total anion current | | Mass analysed anion current | | |
|----------------|---------|-----------|---------------------|--------------------|-----------------------------|--------------------|-----------------------------------|
| | AE (eV) | FWHM (eV) | peak en. (eV) | relative intensity | peak en. (eV) | relative intensity | negative species |
| Nitromethane | 4.0 | 2.8 | | | | | |
| | ≤0.45 | 0.2 | 0.60 | | 0.60 | | NO ₂ ⁻ |
| Nitrobenzene | 4.69 | 0.50 | 4.5 | 88 | — | — | — |
| | 3.79 | 0.50 | 3.8 | 97 | 3.7 | 80 | NO ₂ ⁻ |
| | | | 3.0 | sh. | 2.9 | sh. | NO ₂ ⁻ |
| | 1.36 | 0.40 | 1.25 | 53 | 1.25 | 100 | NO ₂ ⁻ |
| | | | | | 0.7 | sh. | NO ₂ ⁻ |
| | 0.55 | 0.35 | 0.4 | 40 | 0.4 | 4 | M ⁻ |
| | | | 0.00 | 100 | 0.00 | 48 | M ⁻ |
| 2-Nitroanisole | 4.6 | 0.6 | | | | | |
| | 3.88 | 0.55 | 4.0 | 25 | 3.8 | 14 | NO ₂ ⁻ |
| | 1.30 | 0.45 | | | 0.8 | 1 | (M-CH ₃) ⁻ |
| | 0.70 | 0.34 | 0.7 | 50 | 0.75 | 100 | NO ₂ ⁻ |
| | | | | | | | |
| | | | 0.00 | 100 | 0.00 | 11 | M ⁻ |
| 2-Nitrophenol | 4.48 | 0.62 | 4.4 | 66 | 3.6 | 38 | NO ₂ ⁻ |
| | 3.48 | 0.43 | 3.4 | 64 | 3.1 | 100 | (M-OH) ⁻ |
| | 2.75 | 0.60 | 2.7 | 48 | 2.8 | 28 | NO ₂ ⁻ |
| | 1.19 | 0.36 | 1.0 | 81 | 1.1 | 19 | (M-OH) ⁻ |
| | 0.60 | 0.30 | 0.7 | 84 | 0.7 | 13 | (M-OH) ⁻ |
| | | | | | | | |
| | | | 0.4 | sh. | 0.7 | 100 | NO ₂ ⁻ |
| | | | 0.00 | 100 | 0.00 | 8 | (M-OH) ⁻ |
| | | | | | 0.00 | 88 | M ⁻ |

M⁻ designates the molecular anion, sh. a shoulder.

trum (at 0.55 eV) is associated with the non-interacting ring π^* (a_2) component of the benzene π^* (e_{2u}) LUMO, inductively stabilised by the electron-withdrawing nitro group. Its stabilisation (~ 0.6 eV) with respect to the benzene LUMO (AE=1.12 eV [23]) is only slightly smaller than that (0.7 eV) experienced by the filled π (a_2) counterpart with respect to the benzene π (e_{1g}) highest occupied molecular orbital (HOMO), as deduced by the ionisation energy data [3]. It can be noticed (see Fig. 1) that the first resonance shows well-resolved vibrational features, with a spacing of 134 meV. The assignment of the second resonance of the spectrum (1.36 eV) to the b_1 component of the benzene LUMO, destabilised by mixing with the π^* NO₂ orbital, is straightforward. The mesomeric effect of the nitro group overcomes the (strong) inductive effect, which acts in the opposite direction.

Two more narrow resonances, at 3.79 and 4.69 eV, are present in the spectrum, and only the highest-lying empty π^* (b_1) MO of nitrobenzene (with mainly benzene π^* (b_{2g}) character, AE = 4.82 eV in benzene [23]) has not yet been considered. Electron capture into this π^* MO is associated with the resonance at 4.69 eV. In this case, owing to the larger energy gap between the interacting group orbitals and the smaller wave function coefficient at the substituted ring carbon atom, the inductive effect of the nitro group prevails and the net effect is a stabilisation.

The remaining resonance at 3.79 eV thus is not due to simple electron capture into an empty π^* MO. On the other hand, no sharp σ^* resonances are present in the ET spectra of nitromethane and of second-row benzene derivatives. This feature is therefore ascribed to a core-excited shape resonance, that is, electron

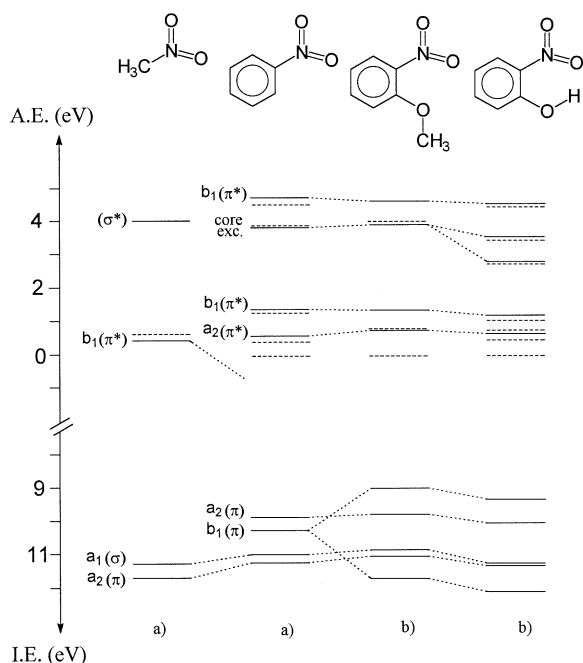


Fig. 2. Diagram of the frontier orbital energies in nitromethane, nitrobenzene, 2-nitroanisole and 2-nitrophenol, as deduced from the ET and photoelectron spectra. Dashed levels represent the energies of the peaks observed in the total anion current. Ionisation energy values taken from a) Ref. 3 and b) Ref. 4.

capture accompanied by a valence electron excitation. Interestingly, to the authors' knowledge, two-electron processes at such a low energy have never been observed in monosubstituted benzenes. The first core-excited resonance detected in benzaldehyde, for instance, has been located at ~ 5.3 eV [11,37]. An analogous valence electron excitation may also accompany core ionisation, the process being referred to as shake-up in the field of X-ray photoelectron spectroscopy. It can be noticed that in nitrobenzene the shake-up process (which involves a $\pi^*(b_1) \leftarrow \pi(b_1)$

Table 2
Vertical EAs (eV) of nitromethane and nitrobenzene and adiabatic EA of nitromethane calculated at the CCSD and QCISD levels, using the D95V+* basis set

| | CH ₃ NO ₂ | | C ₆ H ₅ NO ₂ |
|-------|---------------------------------|--------------------|---|
| | EA _{ad} | EA _{vert} | EA _{vert} |
| CCSD | 0.03 | -0.52 | 0.32 |
| QCISD | 0.06 | -0.45 | 0.37 |

excitation) also occurs at much lower energy than in benzaldehyde [38,39]. These signals were interpreted (and satisfactorily reproduced in energy and intensity) in terms of monopole transitions [38,39], which implies that the filled and empty orbitals involved in the valence transition must possess the same symmetry. By analogy, the core-excited resonance located at 3.79 eV in the ET spectrum of nitrobenzene is ascribed to electron capture into the (b_1) LUMO accompanied by simultaneous LUMO $\leftarrow\pi$ (b_1) excitation [the corresponding transition from the HOMO (a_2) being symmetry forbidden]. The core-excited and the highest-lying resonances (3.79 and 4.69 eV, respectively) would thus both possess b_1 symmetry, so that the two states should be mixed. Consistently, the energy of the latter is ~ 0.3 eV higher than that of the corresponding resonance in benzaldehyde, in spite of the smaller electron-withdrawing effect of the carbonyl group compared with the nitro group.

The AEs measured in 2-nitroanisole are rather close to those of nitrobenzene, the largest shift (0.15 eV) being observed for the first resonance. This destabilisation arises from charge-transfer interaction between the filled oxygen lone pair orbital and the nitrobenzene $\pi^*(a_2)$ empty MO, which has a node at the carbon atom bonded to the nitro group and a maximum wave-function coefficient at the substituted *ortho* carbon atom.

In 2-nitrophenol, strong intramolecular hydrogen bonding occurs, characterised by O...H and O...O nonbonded distances of 1.72 and 2.58 Å, respectively [10]. The measured AEs are close to those of nitrobenzene and of 2-nitroanisole, the main difference at low energy being the stabilisation (0.2 eV) of the second resonance. In agreement, in a previous study of benzaldehyde and 2-hydroxybenzaldehyde [11], interaction of the positively charged hydrogen atom with the acceptor group stabilised the anion states localised at the latter. This effect should thus mainly affect the (not observed) first anion state. There is, however, a macroscopic difference in the ET spectrum of 2-nitrophenol, that is, two core-excited resonances (2.45 and 3.48 eV) are observed below the mainly benzene $\pi^*(b_{2g})$ resonance.

On going from nitrobenzene to the 2-oxy deriva-

tives, the C_{2v} molecular symmetry is lost. In particular, as the HF/6-31G* and D95V* calculations show, while the localisation properties of the empty π^* orbitals remain similar (owing to the absence of low-energy empty orbitals in the oxy substituents), those of the filled π orbitals change drastically (and are governed more by the oxy than by the nitro group). In this sense, the correlation diagram of the filled π MOs reported in Fig. 2 (taken from Ref. [4]) is misleading.

The symmetry reduction allows electron capture into the LUMO to be accompanied by excitation from both the first two occupied π orbitals, at variance with nitrobenzene. In agreement, the energy difference (0.73 eV) between the two core-excited resonances of 2-nitrophenol is very close to the difference (0.79 eV [4]) between the first two ionisation energies (see Fig. 2). Moreover, on going from nitrobenzene to 2-nitrophenol, the second filled π orbital is slightly destabilised [4], and the LUMO should be slightly stabilised by hydrogen bonding (as predicted above). The reduced second HOMO/LUMO energy gap is in line with the lower energy (0.3 eV) of the 3.48 eV core-excited resonance of 2-nitrophenol with respect to the corresponding feature in nitrobenzene. By the same token, of course, an additional low-energy core-excited resonance also should occur in 2-nitroanisole, but for some (not clear) reason, its intensity is too low to allow distinct detection in the ET spectrum.

The empty π^* MO energies were calculated at the HF level using the 6-31G* and the D95V* basis sets, which do not include diffuse functions. The calculated geometries, optimised at the MP2/6-31G** level, closely reproduce the electron diffraction parameters [10]. Fig. 3 reports the D95V* orbital energies. The absolute values (not reported) supplied by the 6-31G* basis set are slightly higher, but the trends remain exactly the same. The calculations were also performed for the conformer of 2-nitrophenol with the hydroxy H atom *anti* to the nitro group. The total energy of this rotamer is predicted to be 9.6 kcal/mol higher than that of the *syn* rotamer (where hydrogen bonding occurs). In the diagram of Fig. 3 all the values were shifted to 1.77 eV lower energy, so that

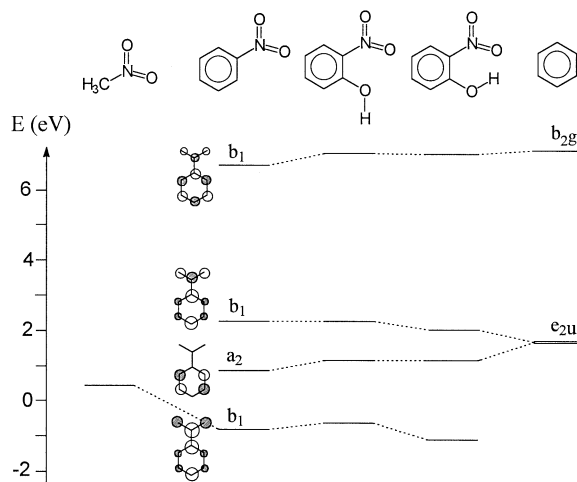


Fig. 3. HF/D95V* empty π^* orbital energies (eV) of nitromethane, benzene and 2-nitrophenol (*anti* and *syn* rotamers). The values (all lowered by 1.77 eV) are normalised to the experimental AE of nitromethane.

the energy of the π^* MO of nitromethane coincides with the measured AE (0.45 eV). As known, at this simple level of theory the calculated empty orbital energies are much higher than the experimental AEs, and the discrepancy increases with increasing energy. However, as previously found in other π systems [11,18,19], the AE trends also are nicely paralleled in the present series. In particular, the destabilisation and the stabilisation of the b_1 and a_2 components, respectively, of the π^* (e_{2u}) LUMO on going from benzene to nitrobenzene are reproduced, as well as the stabilisation of the highest-lying b_{2g} MO. On going from nitrobenzene to the *anti* conformer of 2-nitrophenol, mixing with the oxygen lone pair destabilises the π^* (a_2) MO more than the LUMO, in agreement with the larger wave-function coefficient of the former at the substituted carbon atom. Comparison of the energy variations on going from the *anti* to the *syn* conformers highlights the effects of hydrogen bonding, that is, a stabilisation of the orbitals localised at the nitro group. For the LUMO, this effect overcomes the mesomeric destabilisation due to mixing with the oxygen lone pair. According to the present results, the (positive) EAs of 2-nitrophenol and 2-nitroanisole are predicted to be, respectively, higher and smaller than that of nitrobenzene.

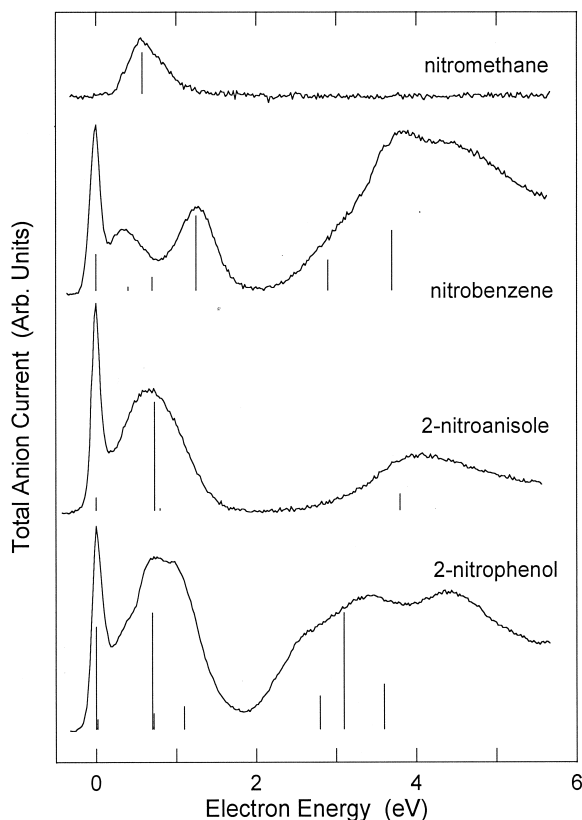


Fig. 4. Total anion current measured at the walls of the collision chamber, as a function of the incident electron energy, in nitromethane, nitrobenzene, 2-nitroanisole and 2-nitrophenol. Vertical lines represent the energies and relative heights of the peaks observed in the mass-selected anion currents.

3.2 Anion production

The total anion current measured at the walls of the collision chamber (0.8 cm from the electron beam) in the four considered nitro derivatives is displayed in Fig. 4. The peak energies observed in these spectra are reported (as dashed lines) in the diagram of Fig. 2, where they are compared with the AEs measured in the ET spectra. The vertical lines in Fig. 4 represent the energies and the relative abundancies (as evaluated from the heights of the signals, within each compound) of the negative species detected through a quadrupole mass filter. The corresponding mass spectra are shown in Fig. 5. All these data are summarised in Table 1.

The total anion current measured in nitromethane in the 0–6 eV energy range shows only one peak, at

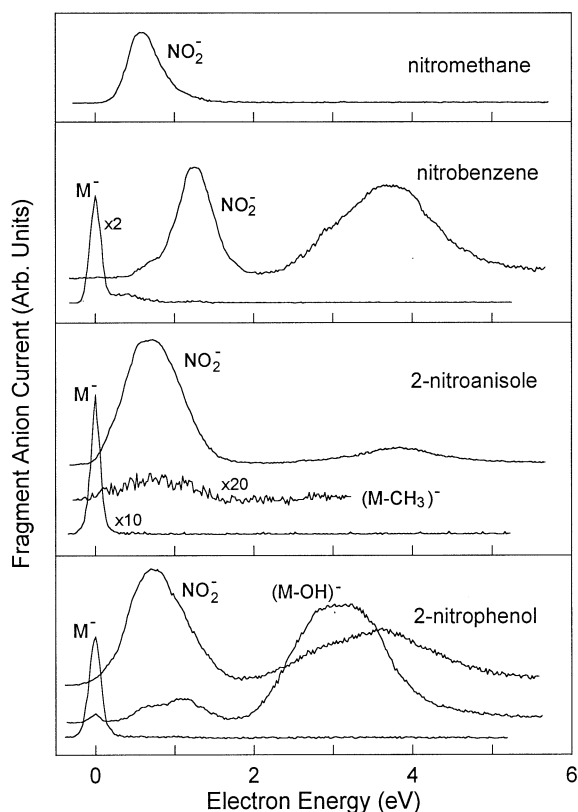


Fig. 5. Mass-selected anion currents, as a function of the incident electron energy, in nitromethane, nitrobenzene, 2-nitroanisole and 2-nitrophenol.

0.60 eV (Fig. 4). The mass-analysed current (Fig. 5) also reveals a single signal, at the same energy, due to the NO_2^- fragment. These findings are consistent with the above assignment of the 0.45 eV feature in the ET spectrum to electron attachment to the π^* LUMO and indicate that this resonance follows a dissociative decay channel. It can be noticed that the anion current peaks at about 0.2 eV higher energy with respect to the centre of the resonance. From the C–N bond energy in nitromethane (2.64 eV [40]) and the EA of NO_2 (2.27 eV [41]), a threshold energy of 0.37 eV can be evaluated for the appearance of the NO_2^- fragment. In the present spectra, the rise of the NO_2^- current is observed at 0.22 ± 0.05 eV.

The total anion current in nitrobenzene displays a sharp peak at zero energy (probably due to the vibrationally excited first anion state) and then one

maximum corresponding to each of the resonances observed in the ET spectrum (see Fig. 2). Mass analysis (Fig. 5) reveals only two negative species, the molecular anion (M^-) and the NO_2^- fragment, and closely reproduces the previous DA data [6]. The molecular anion gives an intense peak at zero energy and a very weak signal at 0.4 eV. The drastic relative intensity reduction of the latter (with respect to the total anion current) indicates that the lifetime of the molecular anion formed through the π^* (a_2) resonance (0.55 eV in the ET spectrum) is barely sufficient for detection through the mass filter, where the required lifetime is of the order of 10^{-6} s. The NO_2^- fragment presents maxima at 1.25 and 3.7 eV and shoulders at 0.7 and 2.9 eV. In nitrobenzene the C-N bond strength is 0.4 eV higher than in nitromethane [40], so that the threshold for NO_2^- production should rise to ~ 0.8 eV. On the basis of energy, the shoulder at 0.7 eV is due to dissociation of the molecular anions formed on the high-energy side of the π^* (a_2) resonance. It can be noticed that transfer of the extra electron from the antisymmetric ring π^* (a_2) MO to the NO_2 group requires a (vibrational) wag motion which reduces the molecular symmetry. The two maxima in the NO_2^- current are clearly associated with electron capture into the second π^* MO of b_1 symmetry (in line with its antibonding character between the nitro group and the ring) and with the core-excited resonance, respectively, while the origin of the shoulder at 2.9 eV is not straightforward.

The total anion current in 2-nitroanisole shows only three features, peaking at 0.00, 0.7 and 4.0 eV. The signals associated with electron attachment to the second (a_2) and third (b_1) empty π^* MOs, well resolved in nitrobenzene, here merge in a single broad peak centred at 0.7 eV. This indicates that the survival time (with respect to electron detachment) of the anions formed on the high-energy side of the latter resonance (1.30 eV in the ET spectrum) is too short for appreciable dissociation to occur. Analysis through the mass filter reveals the molecular anion at zero energy (as found in nitrobenzene), but its abundance, relative to the NO_2^- fragment, is much lower. The NO_2^- current displays an intense and broad peak

at 0.75 eV and a second one at 3.8 eV, that is, very close in energy to the core-excited resonance. A very weak signal at 0.8 eV is also observed, due to the loss of the methyl group from the molecular anion.

In 2-nitrophenol the shape of the total anion current below 2 eV is even more detailed than in nitrobenzene (see Fig. 4). In addition to the zero energy peak, there is a shoulder at 0.4 eV and two unresolved signals peaking at 0.7 and 1.0 eV. At higher energy, three maxima are observed at energies very close to those of the two core-excited resonances and of the highest-lying π^* (b_1) resonance found in the ET spectrum. These features are accounted for by the mass-analysed current, except for the shoulder at 0.4 eV which is ascribed to the (short-lived) molecular anion formed with the π^* (a_2) resonance, in analogy with nitrobenzene. The negative ion mass spectra show intense production of molecular anion at zero energy where a weak signal due to the loss of the OH substituent is also detected. The (M-OH) $^-$ fragment also gives maxima at 0.7 and 1.1 eV, associated with the first and second resonances of the ET spectrum. In the same energy range, the most intense signal is due to a broad (FWHM = 0.8 eV) NO_2^- peak, as found in 2-nitroanisole. Finally, abundant production of both the negative fragments occurs in the energy region of the two core-excited resonances.

In a previous ETS/DAS study [11], the negative ion mass spectra revealed production of the molecular ion at zero energy in 2-hydroxybenzaldehyde, but not in benzaldehyde and in the 3-hydroxy derivative, indicating that intramolecular hydrogen bonding increases the lifetime of the molecular anion. Although in the present compounds the molecular anion is detected even in nitrobenzene and in the 2-methoxy derivative, in 2-nitrophenol the decrease of its relative abundance on going from the total to the mass-selected anion current is much smaller. These findings are perfectly in line with the lifetimes of the molecular anions formed at thermal electron energy determined [7,9] by means of time-of-flight mass spectrometry in nitrobenzene (17.5 μ s), 2-nitroanisole (16 μ s) and 2-nitrophenol (460 μ s).

Acknowledgements

The authors thank the Italian Ministero dell 'Università e della Ricerca Scientifica e Tecnologica for financial support.

References

- [1] L. Sanche, G.J. Schulz, *J. Phys. Rev. A* 5 (1972) 1672.
- [2] K.D. Jordan, P.D. Burrow, *Acc. Chem. Res.* 11 (1978) 341.
- [3] T. Kobayashi, S. Nagakura, *Bull. Chem. Soc. Jap.* 47 (1974) 2563.
- [4] T. Kobayashi, S. Nagakura, *J. Electron Spectrosc. Relat. Phenom.* 6 (1975) 421.
- [5] H.A. Jiménez-Vázquez, M.E. Ochoa, G. Zepeda, A. Modelli, D. Jones, J.A. Mendoza, J. Tamariz, *J. Phys. Chem. A* 101 (1997) 10082.
- [6] L.G. Christophorou, R.N. Compton, G.S. Hurst, P.W. Reinhardt, *J. Chem. Phys.* 45 (1966) 536.
- [7] A. Hadjiantoniou, L.G. Christophorou, J.G. Carter, *J. Chem. Soc. Faraday Transactions II* 69 (1973) 1690.
- [8] L.G. Christophorou, A. Hadjiantoniou, J.G. Carter, *J. Chem. Soc. Faraday Transactions II* 69 (1973) 1713.
- [9] J.P. Johnson, D.L. McCorkle, L.G. Christophorou, J.G. Carter, *J. Chem. Soc. Faraday Transactions II* 71 (1975) 1743.
- [10] K.B. Borisenko, C.W. Bock, I. Hargittai, *J. Phys. Chem.* 98 (1994) 1442.
- [11] A. Modelli, F. Scagnolari, G. Distefano, *Chem. Phys.* 250 (1999) 311.
- [12] N.F. Lane, *Rev. Mod. Phys.* 52 (1980) 29.
- [13] T. Koopmans, *Physica* 1 (1934) 104.
- [14] N. Heinrich, W. Koch, G. Frenking, *Chem Phys. Lett.* 124 (1986) 20.
- [15] M. Guerra, *Chem. Phys. Lett.* 167 (1990) 315.
- [16] J.S.-Y. Chao, M.F. Falcetta, K.D. Jordan, *J. Chem. Phys.* 93 (1990) 1135.
- [17] C.-Y. Juang, J. S.-Y. Chao, *J. Phys. Chem.* 98 (1994) 13506.
- [18] M. Dal Colle, G. Distefano, A. Modelli, et al., *J. Phys. Chem. A* 102 (1998) 8037.
- [19] A. Modelli, F. Scagnolari, D. Jones, G. Distefano, *J. Phys. Chem. A* 103 (1998) 9675.
- [20] J. Cizek, *J. Chem. Phys.* 45 (1966) 4256.
- [21] J.A. Pople, M. Head-Gordon, K. Raghavachari, *J. Chem. Phys.* 87 (1987) 5968.
- [22] L. Sanche, G.J. Schulz, *Phys. Rev. A* 5 (1972) 1672.
- [23] A. Modelli, D. Jones, G. Distefano, *Chem. Phys. Lett.* 86 (1982) 434.
- [24] A.R. Johnston, P.D. Burrow, *J. Electron Spectrosc. Relat. Phenom.* 25 (1982) 119.
- [25] A. Stamatovic, G.J. Schulz, *Rev. Sci. Instrum.* 41 (1970) 423.
- [26] A. Modelli, A. Foffani, F. Scagnolari, D. Jones, *Chem. Phys. Lett.* 163 (1989) 269.
- [27] Gaussian 98, Revision A.6, M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al., Gaussian, Inc., Pittsburgh PA, 1998.
- [28] R. Ditchfield, W.J. Hehre, J.A. People, *J. Chem. Phys.* 54 (1971) 724.
- [29] G.L. Gustev and R.J. Bartlett, *J. Chem. Phys.* 105 (1996) 8785.
- [30] T.H. Dunning, Jr., P.J. Hay, in: H.F. Schaefer III (Ed.), *Modern Theoretical Chemistry*, Plenum, New York, 1976, Chap. 1, p. 1–28.
- [31] F. Ramondo, *Can. J. Chem.* 70 (1992) 314.
- [32] G.D. Parvis III, R.J. Bartlett, *J. Chem. Phys.* 76 (1982) 1910.
- [33] E.P. Grimsrud, G. Caldwell, S. Chowdhury, P. Kebarle, *J. Am. Chem. Soc.* 107 (1985) 4634.
- [34] R.N. Compton, H.S. Carman, Jr., C. Desfrancois, et al., *J. Chem. Phys.* 105 (1996) 3472.
- [35] A. Modelli, *Trends Chem. Phys.* 6 (1997) 57.
- [36] E.C.M. Chen, J.R. Wiley, C.F. Batten, W.E. Wentworth, *J. Phys. Chem.* 98 (1994) 88.
- [37] A. Modelli, P.D. Burrow, *J. Phys. Chem.* 88 (1984) 3550.
- [38] G. Distefano, M. Guerra, D. Jones, A. Modelli, F.P. Colonna, *Chem. Phys.* 52 (1980) 389.
- [39] G. Distefano, M. Guerra, D. Jones, A. Modelli, *Chem. Phys.* 59 (1981) 169.
- [40] D.F. McMillen, D.M. Golden, *Annu. Rev. Phys. Chem.* 33 (1982) 493.
- [41] K.M. Ervin, J. Ho, W.C. Lineberger, *J. Phys. Chem.* 92 (1988) 5405.