The assignment of dissociative electron attachment bands in compounds containing hydroxyl and amino groups.

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Abstract. Dissociative electron attachment (DEA) spectra were recorded for methanol, phenol, diethylamine, tetramethylhydrazine, piperazine, pyrrole and N,N-dimethylaniline. Comparison with HeI photoelectron spectra permitted the assignment of virtually all DEA bands in the saturated compounds to core excited Feshbach resonances with double occupation of Rydberg-like orbitals and various Koopmans' states of the positive ion as a core. These resonances shift to lower energies with alkyl substitution, in contrast to the shape resonances, and are found at surprisingly low energies in the amines. The DEA spectra in the unsaturated compounds show no or only weak evidence for the Rydberg-type Feshbach resonances. It is proposed that DEA in saturated polyatomic molecules containing hydroxyl and amino groups is in general dominated by this type of resonances.

1. Introduction

Boudaiffa *et al* [1] discovered that DNA is damaged by electrons below the ionization energy. The probability of damage (single and double strand breaks) plotted against the energy of the incident electrons showed bands in the $4 - 14$ eV region, reminiscent of dissociative electron attachment (DEA) bands in various molecules. More recently the experiment of Sanche and co-workers has been extended to cover even lower energies and additional bands in the DNA damage (single strand break) have been discovered at ~0.9 and ~2 eV [2]. These two discoveries pointed out that DEA may play a role in radiation damage to living tissue. This assumption has been proven by the observation of electron-stimulated desorption of anions from thin films of DNA [3]. The large size of the DNA molecule and the condensed phase have specific consequences not present in small molecules and a theoretical framework has been proposed to treat these aspects, in particular multiple scattering and diffraction [4]. These discoveries renewed the interest in DEA to isolated polyatomic molecules and in particular to molecules of biological interest [5, 6, 7, 8].

The process of DEA has been extensively studied in the past [9, 10]. Many DEA spectra of polyatomic molecules follow the same general pattern, they can be divided into a low energy domain, between zero and about ~ 5 eV, and a high energy domain, about $5 - 14$ eV.

DEA in the low energy range is generally initiated by an electron capture to form a shape ('one particle') resonance. The initial phase of DEA is characterized by a competition of a very fast autodetachment and a stabilization of the negative ion by a distortion of the molecular frame. The negative ion can then undergo a slower chemical change, which often proceeds on the potential hypersurface of the ground electronic state of the anion. The result may be a simple break of one bond, but also a complex rearrangement ('scrambling') of the atoms to give unexpected products. The bands in the low energy range can often be assigned by their coincidence in energy with resonances found in the electron transmission spectrum (ETS) or vibrational excitation cross sections. Insight into the mechanism can be gained by comparing the appearance energies of the various fragments with the thermochemical thresholds because generally only few dissociation channels are energetically open. The low energy processes in methyl acetate may serve as typical examples [11]. In addition, vibrational Feshbach resonances [12] may serve as doorway states to initiate DEA at very low energies. Examples are CH_3I [13], N_2O [14] and ethylene carbonate [15]. This mechanism has also been proposed for uracil [7].

In virtually all compounds one or several DEA bands are also found in the $5 - 14$ eV range. The assignment of these bands is more difficult because no (or only very weak) corresponding features are found in the other channels of electron scattering, like vibrational excitation or total cross section (as revealed by the ETS). The situation is complicated by the fact that dissociation into many different fragments is energetically possible, and many different fragments often actually occur. These DEA bands have in some cases been assigned to Feshbach resonances with double occupation of Rydberg-like orbitals and a positive ion core [16, 17].

An unambiguous assignment of the high energy bands to such resonances has occasionally been possible in small molecules where the DEA bands have sharp vibrational structure which resembles that of a Rydberg excited state of the neutral molecule (the parent state) and that of the photoelectron band of the positive ion (the grandparent state). Acetaldehyde [18, 19] or ammonia [17] are examples. The situation is more complex in other cases, for example in acetylene, where the DEA band does have vibrational structure, but the band envelope does not resemble that found in the ETS or vibrational excitation cross section [20]. The explanation could lie in an increase of the dissociation rate with vibrational quantum of the resonance. In view of the high energy and the competition with fast autodetachment it is somewhat surprising that complex fragmentations involving 'scrambling' are often observed. They indicate that a relatively long time is available for the dissociation. The mechanism involves propagation of the nuclear wave packet on a manifold of the Rydberg-like anion states, possibly predissociated by repulsive valence states, as recently explicitly calculated for

water [21]. The analogy of conical intersections [22, 23] is likely to be involved.

Feshbach resonances with occupation of Rydberg-like orbitals are well known from scattering experiments other than DEA, in particular ETS of rare gases, diatomic and polyatomic molecules [24, 25, 26, 27] or in the vibrational excitation cross sections (for an example, see [28]). The energies of these Feshbach resonances were found to have a simple relation to the energies of the parent Rydberg states and the grandparent state of the cation. The relation depends only weakly on the molecule in question. The electron affinity of the parent Rydberg state is of the order of $0.3 - 0.5$ eV for the s^2 configuration [24, 25, 26, 27, 29]. Read expressed the relation with a modified Rydberg-Ritz formula [30]. Spence [31] fitted a linear relationship between the energy of the Feshbach resonance E_F and the first ionization energy I, $E_F = A \cdot I + B$, for many hydrogen- and methyl-halides. The slope A had the values of 1.02 and 0.93 for the s^2 and p^2 configurations, respectively. That is, for the purpose of the present work, the slope can be taken as equal to 1. The constant B had the values -3.9 and -1.8 eV for the s^2 and p^2 configurations, respectively. This means that the s^2 Feshbach resonance was always found $\sim$4 eV below its grandparent state, the ground state of the ion.

Jungen *et al* [32] extended the Feshbach resonance assignment to excited grandparent cation states. They studied the relation of the three DEA bands in H_2O to the three lowest Koopmans' states of the cation and recognized that the pattern of the ionization energies matches that of the DEA bands. Based on this match, they assigned the DEA bands to the $^2(1b_1, 3s^2)$, $^2(3a_1, 3s^2)$ and $^2(1b_2, 3s^2)$ Feshbach resonances (expressed using the notation of Robin [16] which indicates the multiplicity, the orbital from which an electron has been removed, and then the additionally occupied orbital, separated by a comma). The configuration of H_2O is $^1(1a_1^2\ 2a_1^2\ 1b_2^2\ 3a_1^2\ 1b_1^2)$. The energy difference between the resonances and the grandparent cationic states was larger (5.6 eV for the lowest state) than that found for the rare gases or the halides in connection with the transmission spectroscopy, but the matching patterns of the DEA bands and the ionization energies permitted a convincing assignment of the three DEA bands.

For completeness it should be mentioned that in an intermediate energy range, $\sim 4 - 7$ eV, DEA bands have been found which have nearly the same energy as, and resemble in shape, the low-lying singlet valence excited states of the target molecule. These bands have been found in unsaturated compounds and assigned to resonances where an s-like electron is weakly bound to a valence-excited core. Examples are CS_2 [33] and other molecules [34].

The present work investigates whether there are matches between the photoelectron spectra and the DEA spectra of several polyatomic molecules which contain hydroxy- and amino- groups, which would indicate that the high energy DEA bands are due to to Feshbach resonances with double occupation of Rydberg-like orbitals.

2. Experiment

The dissociative electron attachment spectrometer used to measure the yield of mass-selected stable anions as a function of electron energy has been described previously [15, 35, 36]. It employs a magnetically collimated trochoidal electron monochromator to prepare a beam of quasi-monoenergetic electrons, which is directed into a target chamber filled with a quasi-static sample gas. Fragment anions are extracted at 90° by a three-cylinder lens and directed into a quadrupole mass spectrometer. This scheme is known to detect slow ions more efficiently than fast ions. It is a general experience, however, that polyatomic fragments represent a very efficient sink for excess energy and substantial kinetic energy release is thus very unlikely with the large molecules studied here. The spectra were calibrated on the onset of the O^-/CO_2 signal. The electron current was several nanoamperes and the resolution about 70 meV. The instrument is not capable of detecting H^- and this fragment is therefore excluded from the present study. The photoelectron spectra were recorded with a modified Perkin Elmer PS18 HeI photoelectron spectrometer.
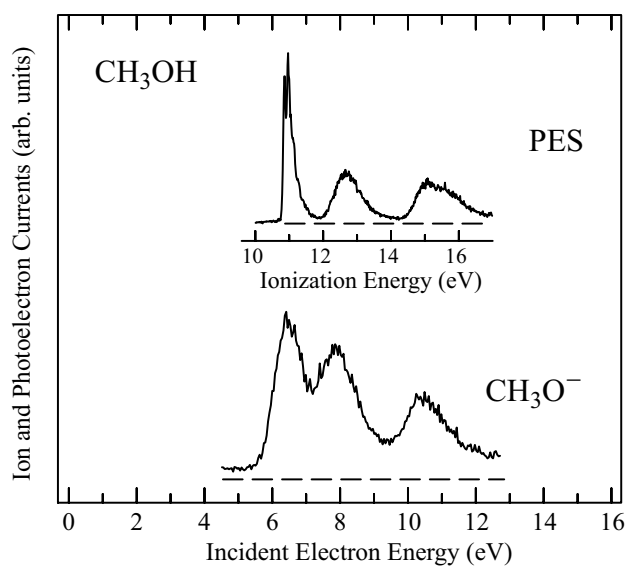
3. Results and Discussion

Figure 1. Comparison of the photoelectron spectrum (shown shifted by -4.5 eV) and the DEA spectrum in methanol.

3.1. Methanol

Kühn *et al* [37] studied dissociative electron attachment to methanol including fully and partially deuterated isotopomers. They also analyzed the translational energies of the ionic fragments. They observed CH_3O^-, OH^- and O^- fragments (with relative

intensities 10, 14 and 100, respectively) and three bands in the $5 - 12$ eV range which they assigned to core excited resonances with two electrons in a Rydberg-like MO. The observation of unexpected fragments from the isotopically substituted compounds, i.e., OH^-/CH_3OD or OD^-/CD_3OH revealed hydrogen scrambling for these two fragments, in contrast to the formation of CH_3O^- (and its deuterated analog), which proceeded without scrambling.

Figure 1 compares a DEA spectrum of methanol with the photoelectron spectrum, shifted by -4.5 eV. There is a correspondence of patterns between the three DEA bands and the three lowest photoelectron bands, reminiscent of that found for water [32]. In analogy to water we thus assign the three DEA bands to Feshbach resonances with a double occupation of a $3s$ Rydberg-like orbital and the lowest three Koopmans' states of the cation as a core. The three states of the cation (the grandparent states) have an electron removed from the $2a'' \; n_0$ nonbonding orbital (essentially an oxygen p orbital perpendicular to the COH plane), the $7a' \; \bar{n}_0$ orbital (essentially an oxygen p orbital in the COH plane), and the $6a' \; \sigma_{CO}$ orbital [38, 39]. The electron configurations of the resonances can then be written as $^2(2a'', 3s^2)$, $^2(7a', 3s^2)$ and $^2(6a', 3s^2)$.

The CH_3O^-/CH_3OH spectrum is remarkably similar to the HO^-/H_2O spectrum [32] in its shape, but the bands are shifted to lower energies by about 0.5 eV. This is consistent with the present assignment of the resonances. Alkyl substitution is well known to destabilize occupied orbitals and thus to lower the ionization energies [38]. This leads to lower energies of the Feshbach resonances. Note that this trend is exactly opposite to that found for a shape resonance where alkyl substitution destabilizes the energy of the orbital temporarily occupied in the resonance, thus rising its energy. This difference of trends is a helpful tool for distinguishing the two types of resonances.

The energy difference between the daughter resonance and the grandparent ion states is about 4.5 eV for all states in methanol, slightly larger but similar to the difference found by Spence [31] for molecules which are only remotely related. The difference is substantially smaller than in water. This is surprising in view of the fact that a difference of about $3.8 - 4.6$ eV seems to be universal both in the work of Spence and in the present work.

3.2. Diethylamine

The parent compound ammonia has already been studied by Stricklett and Burrow [17] who assigned the prominent DEA band at 5.65 eV to the $^2(1a_2'', 3s^2)$ Feshbach resonance, based on the comparison of the DEA band with the parent Rydberg band (obtained from an electron energy loss spectrum) and the photoelectron band. The difference of the daughter and the grandparent states is thus 5.2 eV (the first vertical ionization energy being 10.85 eV [38]).

Figure 2 compares the yield of two anion fragments, $(M - H)^-$ (loss of an H atom) and $C_2H_5NH^-$ (loss of an ethyl group), with the photoelectron spectrum of diethyl amine. In an analogy to the assignment of Stricklett and Burrow [17] we assign the
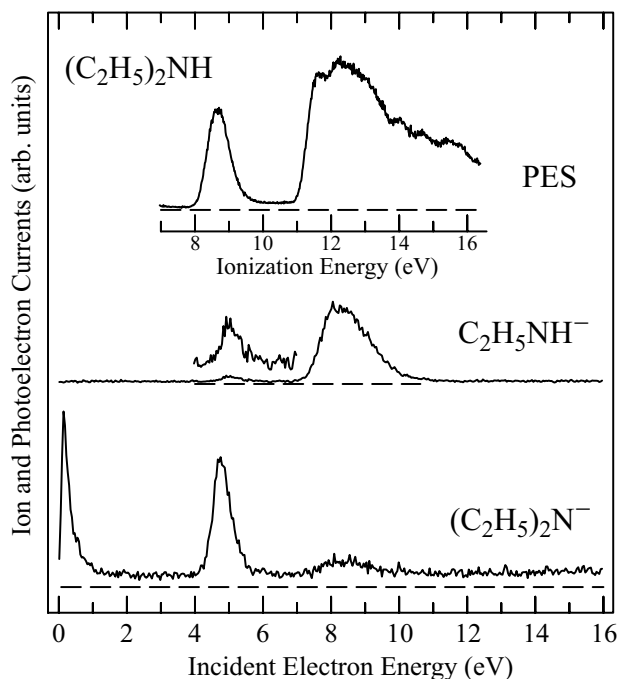
Figure 2. Comparison of the photoelectron spectrum (shown shifted by -4.0 eV) and the DEA spectra in diethylamine.

4.7 eV DEA band to the $^2(n_N, 3s^2)$ Feshbach resonance where n_N is the a' nonbonding 'lone pair' orbital. There are several interesting aspects about this DEA band. It is unusually low for a Feshbach resonance, because of the very low ionization energy of an amine. The fact that it shifted down in comparison to ammonia supports its assignment. The band is unexpectedly narrow (0.63 eV at half height), narrower than the photoelectron band (0.75 eV at half height). This is in contrast to ammonia, where the DEA and photoelectron bands have about equal widths.

There is a correspondence between the second photoelectron band and the 8.4 eV DEA band, which can consequently be tentatively assigned to the $^2(\pi_{CH_3}, 3s^2)$ Feshbach resonance, where π_{CH_3} is the a'' pseudo π orbital [39], contributing primarily to the C-H bonds. The photoelectron bands above about 13 eV do not have counterparts in the DEA spectra, possibly because of very short autodetachment lifetimes of the resonances.

The energy difference between the daughter resonance and the grandparent cation is about 4 eV for diethylamine. This is less than in ammonia – the situation thus resembles that of the oxo compounds where the difference in water was larger than that in methanol.

The peak at ~ 0 eV in the yield of the $(M - H)^-$ anion cannot be the result of DEA to an isolated molecule because it lies below the dissociation threshold. We do not understand its origin in detail.
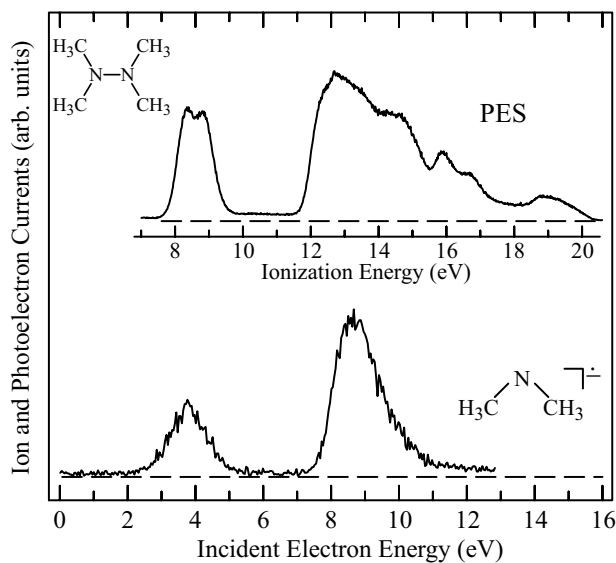
Figure 3. Comparison of the photoelectron spectrum (shown shifted by -4.6 eV) and the DEA spectrum in tetramethylhydrazine.

3.3. Tetramethylhydrazine

The yield of the $(CH_3)_2N^-$ anion, shown in the lower part of the figure 3, exhibits two bands peaking at 3.77 eV and 8.67 eV.

Photoelectron spectra of various diamines, hydrazines and diazirines have been extensively studied because of the relation of the splitting of the n_+ and n_- lone pair bands to the conformation of the compounds (twist angle along the N-N bond) and the competition of the 'through-space' and 'through-bond' interactions [40, 41, 42, 43]. Tetramethylhydrazine has two amino groups linked together. The ensuing conjugation and through-bond interaction lead to a splitting of the n_+ and n_- orbitals and the corresponding photoelectron bands by 0.46 eV (table 1).

The 3.77 eV DEA band does not have a double maximum. The DEA profile appears to be broader than the photoelectron band, either because of lifetime broadening or because of a wider Franck-Condon profile. We thus do not know whether only one or both of the n_+ and n_- cation states have a DEA band associated with them, and whether it would be more appropriate to show the photoelectron spectrum such that the DEA band coincides with the lower, or the center of both photoelectron bands. The photoelectron spectrum in figure 3 has been shifted to bring the lower of the two photoelectron bands into coincidence with the peak of the DEA band. The general observation, that there is a correspondence between the photoelectron and the DEA spectra, does not depend on which way they are compared, however.

The photoelectron spectrum above 12 eV consists of several overlapping bands corresponding to ionization from various σ orbitals. The onset around 12 eV and the first peak, around 13 eV, correspond quite well to the 8.67 eV DEA band. The photoelectron bands above about 14 eV do not have corresponding bands in the DEA

spectrum, however.

The photoelectron spectrum of tetramethylhydrazine resembles that of the parent compound hydrazine, where the n_+ and n_- ionization energies are 9.91 and 10.64 eV, respectively [45], except that the fourfold methyl substitution shifts the two bands to lower energies by ~ 1.5 eV. An NH_2^- band has been reported at 5.8 eV in the DEA spectrum of the parent compound hydrazine [44]. The difference of the first ionization and the attachment energy is thus ~ 4.1 eV, in line with the differences observed for the compounds studied here.
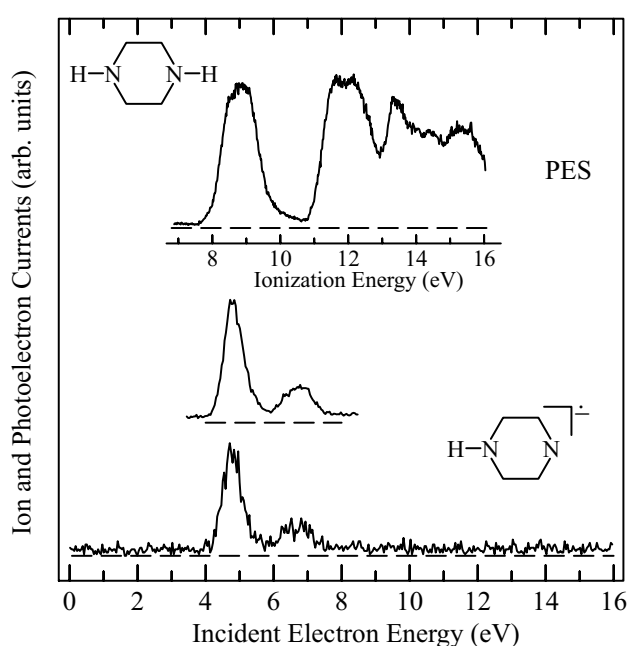
3.4. Piperazine

Figure 4. Comparison of the photoelectron spectrum (shown shifted by -3.8 eV) and the DEA spectrum in piperazine. The insert shows a spectrum with an improved signal/noise ratio.

The yield of the $(M-H)^-$ anion in piperazine is shown in figure 4. It exhibits two fairly narrow bands peaking at 4.8 eV and at 6.7 eV. The first photoelectron band of piperazine does not have two separate maxima like that of tetramethylhydrazine, but its shape has a somewhat 'flat' top and permits to identify two values, 8.62 and 8.97 eV, for the vertical n_- and n_+ ionization energies. (Our results do not agree with the values of 8.98 and 9.53 eV reported previously [42].) As in the case of tetramethylhydrazine, the n_-/n_+ splitting observed in the photoelectron spectrum does not appear in the DEA spectrum and we have chosen to show the photoelectron spectrum shifted such that the lower ionization energy coincides with the peak of the DEA band. In the case of piperazine this choice is also more compatible with the observed band widths.

The second DEA band does not have a corresponding band in the photoelectron spectrum, but we note that it has the right energy to be assigned to the p^2 configuration with the ground state ion as a core. This DEA band lies $\sim$1.9 eV below the first ionization energy in piperazine, which is close to the value of 1.8 eV found for the p^2 resonances in hydrogen- and methyl-halides by Spence [29].

Table 1. Vertical ionization energies I_v, energies of the first DEA bands E_F, and their differences $\Delta E_{IF} = I_v - E_F$ (all values in eV). Two ionization energies, for n_- and n_+, are given where applicable. Only the lower one is taken to calculate ΔE_{IF}.

compound	I_v		E_F	ΔE_{IF}
methanol	10.95[a]		6.45	4.5
diethyl amine	8.70		4.70	4.0
tetramethylhydrazine	8.36	8.82	3.77	4.6
piperazine	8.62	8.97	4.80	3.8

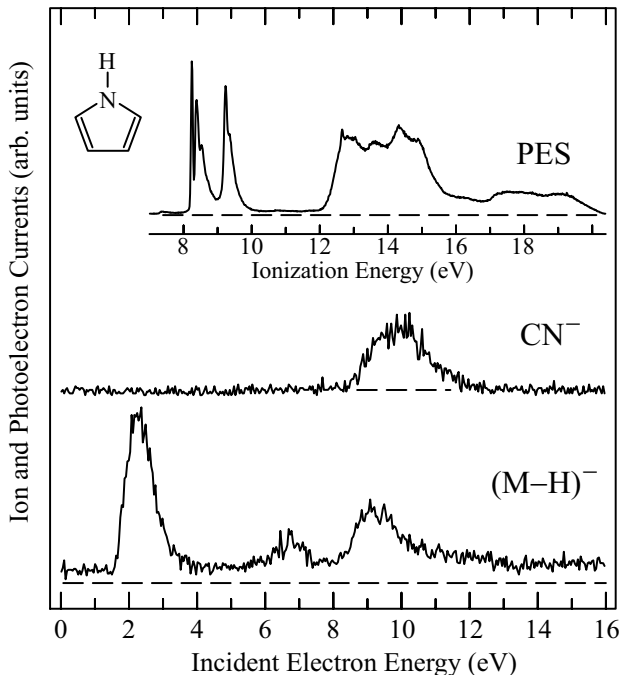[a] $0-0$ transition at 10.85 eV.

3.5. Pyrrole

Figure 5. Comparison of the photoelectron spectrum (shown shifted by -4.4 eV) and the DEA spectrum in pyrrole.

The $(M-H)^-$ yield and the CN^- yield in pyrrole are compared to the photoelectron spectrum in figure 5. The anion yields are in agreement with the data recorded at a higher sensitivity (but lower resolution) by Muftakhof *et al* [50], except that they

additionally report several very weak bands in the yield of various fragments. In particular, they report very weak bands at 5.0 and 5.8 eV in the (M−H)$^-$ yield. The most prominent DEA band peaking at 2.25 eV can be assigned to the lowest π^* shape resonance known from ETS [46, 47, 48] and vibrational excitation cross sections [49].

The first two ionization energies are $I_1 = 8.25$ eV and $I_2 = 9.24$ eV. Feshbach resonances with double occupation of Rydberg-like orbitals would thus be expected around 3.9 and 4.8 eV. As no such bands are observed in the DEA spectra we conclude that the Feshbach resonances of the type discussed in this paper either do not occur, or they do not play a significant role in DEA. They could be too strongly perturbed by the valence $^{1,3}(\pi, \pi^*)$ states present in this energy range. This would be in line with the interpretation of Muftakhof *et al* [50], who assign the very weak 5.0 and 5.8 eV bands in their spectra to resonances with valence excited states as parents. The DEA bands in the $9-10$ eV region correlate loosely with the photoelectron bands in the $12-16$ eV region and could be assigned to Feshbach resonances with holes in the deeper orbitals, but the evidence is not as strong as for the saturated compounds discussed above.

3.6. Phenol and N,N-dimethylaniline

We also measured the DEA spectra of phenol and N,N-dimethylaniline and compared them with the photoelectron spectra. The DEA spectra are dominated by the lowest π^* shape resonance in both compounds. The phenolate anion yield from phenol exhibits two weak and very broad ($\sim$1.5 eV wide at half height) bands around 6.2 and 8.7 eV, whose separation is reminiscent of that of the photoelectron bands, but the correspondence is not convincing because of the large widths of the DEA bands. We did not observe any DEA bands above the 1.2 eV shape resonance in dimethylaniline. No DEA bands can thus satisfactorily be assigned to Rydberg-type Feshbach resonances in these two compounds.

4. Conclusions

Virtually all dissociative electron attachment bands in methanol and the saturated amines studied here could be assigned to Feshbach resonances with double occupation of Rydberg-like orbitals. The assignment is based on three arguments:

- The energetic relation of the resonances to their grandparent cation states. The energy differences lie in the range $3.8 - 4.6$ eV in the present work, comparable to the value 3.9 eV found by Spence [29] for methyl and hydrogen halides.
- The correspondence of the band patterns of the DEA and the photoelectron spectra, relating excited states of the ion to higher DEA bands.
- The way in which the DEA bands shift upon alkyl substitution or presence of two amino groups, coupled by 'through space' and 'through bond' interactions. The trend expected for Feshbach resonances and found here is opposite to that found for shape resonances.

These are the arguments used previously to assign resonances in the ETS of rare gases, diatomic and triatomic molecules and hydrocarbons by Sanche and Schulz [24, 25, 26, 27], in the ETS of methyl and hydrogen halides by Spence [29], and in the DEA in ammonia by Stricklett and Burrow [17]. The arguments are slightly expanded here to include the trend in alkyl substitution and lone-pair interaction.

An essential part of the argument is the assumption that for this type of Feshbach resonances the energy difference between the resonance and the grandparent depends only weakly on which molecule is the target, because the Rydberg-like orbitals are diffuse and penetrate the core only weakly. The energy differences found experimentally do cover an appreciable span, however. The argument of the constant energy differences would thus not be sufficient for the present compounds, but we believe that all three above arguments combined provide a convincing evidence for our assignment. It appears that the degree of penetration of the Rydberg-like orbitals into the core is not negligible and varies from molecule to molecule.

The magnitude of the energy splitting indicates an s^2 configuration in nearly all cases. This resembles the situation in H_2O, where only the (structureless) s^2 resonances were found in DEA [32], although a p^2 resonance with vibrational structure was identified at higher energy in the ETS [27]. Only the 6.7 eV DEA band of piperazine could be due to a p^2 configuration.

The situation is different in the unsaturated compounds phenol, pyrrole and N,N-dimethylaniline, where no or only very weak bands could be assigned to Feshbach resonances with double occupation of Rydberg-like orbitals. The prominent DEA bands in these compound are due to shape resonances (with single occupation of a 'virtual' valence orbital) or to core excited resonances with valence orbitals. The decisive difference between the two classes of compounds appears to be the presence of low-lying valence π^* virtual orbitals in the unsaturated compounds. The low-lying valence excited states which are a consequence of the π and π^* orbitals and which are absent in the saturated compounds appear to interfere with the Rydberg-type Feshbach resonances in DEA.

The DEA bands are generally broader than the photoelectron bands. The first photoelectron band in methanol has sharp vibrational structure which is missing in the DEA band. This is not automatically the case in all molecules, the DEA bands due to Feshbach resonances in ammonia [17] or acetaldehyde [18, 19] do have vibrational structure. The first DEA in diethylamine is not broader, but even slightly narrower than the photoelectron band. This would indicate that the change in width is at least in part caused by different Franck-Condon profiles. The width of the diethylamine photoelectron band is caused primarily by the broad Franck-Condon envelope due to strong excitation of the 'umbrella' vibration, a consequence of the fact that the neutral molecule is pyramidal but the cation is planar around the N-atom. The narrower width of the DEA band could thus indicate a narrower Franck-Condon profile which would result if the Feshbach resonance would be slightly pyramidal, closer to the neutral molecule in terms of geometry than the cation.

The $n_+ - n_-$ splitting is clearly seen in the photoelectron spectrum of tetramethylhydrazine, and, slightly less clearly, in piperazine, but appears to be smeared out by the broadening in the DEA band. It thus can not be decided whether both or only one of the n_+ and n_- states give rise to DEA bands. In this respect it would be interesting to study diamines such as 1,4-diazabicyclo[2,2,2]octane (DABCO), with a larger splitting of the n_- and n_+ orbitals and consequently photoelectron bands ($I_1 = 7.52$ eV, $I_2 = 9.65$ eV [41]), and see whether DEA bands corresponding to both of these states will be observed.

It can be expected that the Rydberg-type electrons of the resonances identified here are to some degree localized around the electron hole of the core, that is, around the -OH and the -NH$_2$ groups for ionizations from the nonbonding orbitals. That means that very similar resonances can be expected generally in molecules having an -OH group attached to a sp^3 hybridized carbon, for example the sugar constituent of a nucleic acid. This expectation appears to be confirmed by the very recent DEA spectrum of a nucleoside [51]. The same could be true for larger molecules containing the amino group. These resonances could dominate DEA even in condensed media, although they may be perturbed and shifted to higher energies because of their large spatial extent, in a way similar to that found for Rydberg states of neutral molecules [16]. Multiple scattering and ensuing diffraction have also been shown to effect the capture in the very large molecule of DNA [4].

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