Coupling between dipole-bound and valence states: the nitromethane anion

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Nitromethane is a prototypical example for a molecule that can bind an extra electron in two fundamentally different ways forming dipole-bound as well as valence anions. The classification of the electronic states as dipole-bound or valence does in fact suggest a diabatic viewpoint, and we investigate the coupling between these two electronic states of the nitromethane anion. The coupling element W is extracted from a cut through the two lowest adiabatic potential energy surfaces by fitting of a simple avoided crossing model potential, that is, W is effectively approximated as half the smallest splitting. High level *ab initio* calculations are performed to compute the two states along the cut. We discuss in particular how a balance between the two very different electronic states can be achieved, and how the temporary nature of the valence anion in a large region of the relevant nuclear coordinate space can be taken into account. The autodetachment lifetime following vertical electron attachment to the neutral is computed, but the calculation of the temporary anion state turns out to be too expensive for a study of the two adiabatic surfaces, and consequently, the second adiabatic state is only included at geometries where it lies below the neutral potential energy surfaces. We find a coupling matrix element of 30 meV. On the one hand, this value is much smaller than the vertical excitation energies underlining the need for a diabatic picture. On the other hand, this value suggests rapid transitions on a mass spectrometric timescale substantiating the notion that the dipole bound state provides an efficient doorway for attachment to the valence state.

1 Introduction

A large class of polar molecules can bind electrons in two fundamentally different ways.[1–4] On the one hand, these molecules can form dipole-bound anions where the extra electron is essentially attached to the electrostatic dipole potential of the neutral system. The associated binding energies are small, and the dipole-bound electron occupies an extremely diffuse orbital where the average distance to the molecular framework is typically >10 Å. On the other hand, the extra electron can occupy a compact valence orbital, and a stable, conventional or valence anion is formed. For this type of system a number of questions arise pertaining to which type of anion is formed under which conditions, and to what extent the two anionic states can be converted into each other. Examples that have recently been investigated include nitromethane,[5] nitrobenzene,[6] uracil,[7] and the thymine dimer.[8]

In particular, the diffuse dipole-bound states have been discussed as providing 'doorways' for the formation of the stable valence states (see ref. 5, 6, 9–12 and references therein), or, in cases where the valence state is dissociative, as doorways for dissociative attachment processes (see *e.g.* ref. 13, 14). In this context it is convenient to adopt a diabatic picture, that is, one analyses the system in terms of electronic states that retain their character when the nuclei move. Indeed, the distinction of dipole-bound and valence states as such, does in fact imply a diabatic viewpoint. We will discuss the concept of diabatic states in more detail below, at this point we only note that diabatic states are coupled through the electronic Hamiltonian, and, loosely speaking, the coupling matrix element is responsible for transitions between the states and provides a measure to what extent the 'doorway' is actually open.

Nitromethane represents the prototypical example of an anion that possesses both a dipole-bound and a valence state, and both anionic states as well as their coupling are experimentally well documented[5,10,11,15,16] (for references to earlier work see ref. 5). Photoelectron spectra of $CH_3NO_2^-$ ions formed in supersonic sources show only evidence of a valence state, but, a mixture of anions exhibiting dipole-bound as well as valence character is produced by Rydberg electron transfer. The experimental values of the electron affinities (EA) are 12 ± 3 meV for the dipole-bound and 260 ± 80 meV for the valence state, and a coupling between the two anionic states has been inferred from the Rydberg quantum number dependence of both attachment rate and field detachment signal.

In this paper we investigate the coupling between the two anionic states of nitromethane theoretically. So far, the "coupling" and "transitions" between the two nitromethane anions have mostly been discussed in terms of the barrier on the lowest Born–Oppenheimer potential energy surface (PES).[5,9,10] In other words, an adiabatic picture has been adopted, and *ab initio* calculations have only been performed for the lowest adiabatic state.[9] Here, we emphasise the diabatic viewpoint and the coupling between the *two* electronic states. In particular, we compute a cut through the *two* relevant adiabatic PES, and approximate the coupling matrix element effectively by half of the smallest splitting. The paper is organised as follows. In section 2 we discuss briefly the notion of adiabatic and diabatic PES in the context of anions possessing both a dipole-bound and a bound valence state. Moreover, the extraction of the coupling matrix element from our *ab initio* data using a primitive diabatisation scheme is described. The main body of the paper is section 3 where bound state *ab initio* calculations for the two anionic states are discussed. Special

emphasis is placed on obtaining a balanced description, and the possible autodetachment from the upper state. Results for a cut through the two lowest adiabatic PES are presented, and from these data the coupling matrix element is extracted. In section 4 the lifetime of the temporary anion state originating from vertical attachment of a valence electron is considered, and our conclusions are summarised in section 5.

2 General considerations

In this section we start with a brief review of the notion of adiabatic *vs.* diabatic states (a very readable introduction can be found in ref. 17) and put it into the present context. To be specific, the nitromethane anion is employed as an example, but the ideas apply to a large class of molecular systems. Then the calculation of the coupling between the diabatic dipole-bound and valence states using *ab initio* methods is discussed, and our 'primitive' diabatisation scheme is described.

In the context of Born–Oppenheimer potential energy surfaces, it is straightforward to say what the adiabatic states are, namely the eigenstates of the electronic Hamiltonian $H_e = H - T_n$, where H is the full Hamiltonian of the molecule and T_n is the kinetic energy operator of the nuclei. For an anion as nitromethane, the lowest adiabatic PES will show two minima corresponding to the dipole-bound and to the valence anions, respectively (see Fig. 1 for a schematic representation). In going from one minimum to the other the nature of the electronic wavefunction ϕ changes dramatically, and provided the change occurs sufficiently rapidly, the derivative coupling elements (essentially $\langle \psi | \sum \partial / \partial Q_i | \phi \rangle$ terms where Q_i are the nuclear coordinates) will show substantial values, and the Born–Oppenheimer approximation breaks down.

Whenever an adiabatic electronic state depends strongly on the nuclear coordinates in the sense that the derivative coupling terms are large, it is conceptually as well as computationally of great advantage to use diabatic states, that is, electronic states that do not change character within the relevant nuclear coordinate range (see ref. 17, 18 and references therein). Within a basis of diabatic states the electronic Hamiltonian is not diagonal. The diagonal elements $(H_e)_{ii}$ define the diabatic PES, and the off diagonal elements $(H_e)_{i \neq j}$ are referred to as the coupling matrix elements. In this way the kinetic coupling through T_n can be minimised and neglected, and one has instead a potential coupling that is much easier to handle.
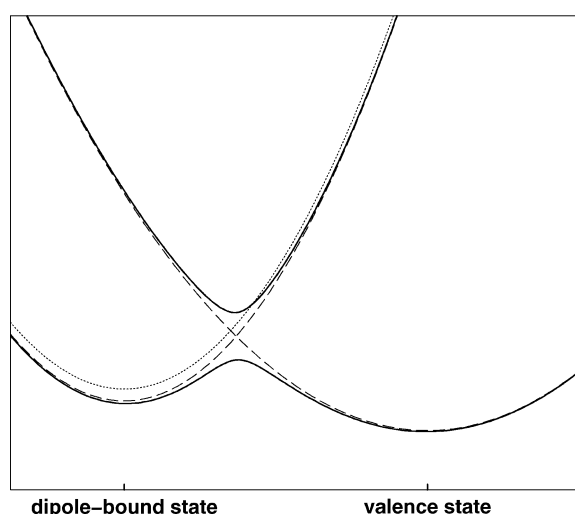
Fig. 1 Schematic representation of the adiabatic (full lines) and diabatic (dashed lines) PES of an anion possessing both a dipole bound and a valence state. In addition the PES of the corresponding neutral molecule is indicated (dotted line). Note that at any fixed geometry anionic states above the neutral PES are resonances with complex valued PES.

In contrast to the adiabatic representation, the definition of diabatic states is in general non-unique (for a discussion of different diabatisation schemes see ref. 18 and references therein; a good starting point for more recent work is ref. 19), but the physics of the problem often suggests a meaningful choice (see *e.g.* ref. 17). In the present context this choice is rather obvious, since the classification as dipole-bound or valence anion provides a natural definition of the diabatic states. The dipole-bound and the valence state of the nitromethane anion will clearly cross along a cut through the two minima (Fig. 1), and, transitions or, loosely speaking, hopping between the two anionic states will be determined by the coupling matrix element.

Thus far we have a typical two state avoided crossing situation which is very well known. The coupling between a dipole-bound and a valence state is more complicated because of the possible autodetachment, that is, because of the coupling with the PES of the neutral (Fig. 1). From any vibrational state of the anion that is above the vibrational ground state of the neutral system an electron can be ejected, and at any fixed geometry the electronic states of the anion that lie above the neutral correspond to resonance or temporary states. The additional coupling to the neutral surface can have a profound influence on the effective coupling between the anionic states, and we will come back to this point in section 4.

While it is in principle possible to compute the two multidimensional anionic PES including their mutual coupling and the autodetachment width, this task is very cumbersome and at the moment effectively impossible. Here, as a first approach to the system we aim at a reasonable estimate for the coupling between the anionic states that will allow us to draw some qualitative conclusions. Specifically, a one-dimensional cut including the crossing of the diabatic states is defined in the next section, and the adiabatic surfaces along the cut are computed using high level *ab initio* methods. Our results are then used for a least squares fit of a simple avoided crossing model potential

$$V = \begin{pmatrix} V_1 & W \\ W & V_2 \end{pmatrix}, \qquad (2.1)$$

where the diagonal terms are harmonic potentials in the coordinate s defining the cut

$$V_i = \frac{1}{2} \omega_i (s - s_i)^2 + v_i, \qquad (2.2)$$

and the off diagonal coupling element W is assumed to be constant. This approach is effectively equivalent to approximating the coupling as half of the smallest splitting along the given cut through the adiabatic surfaces, which is however – owing to the possible autodetachment – difficult to pinpoint (*cf.* Fig. 1). Moreover, this procedure allows us to investigate more sophisticated *ansaetze* for W in a straightforward manner.

In the particular case of the nitromethane anion, we expect that an one-dimensional approach in the spirit of Fig. 1 represents an adequate framework for qualitative considerations. The two electronic states in question do have the same symmetry ($^2A'$), there is no high symmetry point where the coupling does vanish, and the two vibrational modes that are expected to be most relevant – NO_2 wagging and symmetric NO stretching[9] – are both totally symmetric. Let us point out, that apart from other avoided crossing situations, the one-dimensional potential V is in particular equivalent to model Hamiltonians used in electron transfer theory,[20] and indeed, one can view the dipole-bound/valence state dynamics as an intramolecular electron transfer process.

3 Bound state *ab initio* calculations

From an electronic structure viewpoint computing the *two* lowest PES of the nitromethane or similar anions poses a

challenging task for two reasons. On the one hand, one needs to describe two very different electronic states in a balanced way, and, on the other hand, in a considerable fraction of nuclear coordinate space the second state represents a resonance or temporary species, and one needs to include the possible electron autodetachment by some mean. We defer the latter issue to section 4, and in this section only those parts of the two anionic PES are considered that lie below the neutral surface.

The balance issue deserves careful consideration, since it is well established that the electronic structures of the two anionic states are notably distinct. The orbitals of a dipole-bound state are very similar to those of the neutral molecule, whereas the orbitals of an anionic valence state differ dramatically from this set. Thus, separate high level calculations for the two states can be performed in a straightforward way using the respective orbital set, but, if one aims at describing both states within one calculation, which orbital set should be employed? To be specific consider a configuration interaction (CI) calculation for the two anionic states. If the orbitals of the neutral molecule are used to build the configuration space, just one reference configuration is needed to include the dipole-bound state, but one needs many reference configurations to account for the orbital relaxation of the valence state. Obviously, the opposite is true if the CI expansion is based on the orbitals of the valence state, and, if averaged orbitals were used, one probably needs several references for both states. Apart from the necessity to perform an extensive multireference CI (MRCI), it is by no means clear how exactly a reasonably balanced CI space can be constructed. We will discuss different CI spaces in the next section where MRCI wavefunctions are employed to compute the lifetime of the temporary $CH_3NO_2^-$ anion. Let us at this point only note that the balance requirement leads to huge, effectively impractical CI expansions.

A different strategy to achieve a balanced description of the two anionic states is to use propagator based or closely related methods (see *e.g.* ref. 21, 22). Examples include the ADC,[23] the EOM,[24] and the EOM-CC[25] methods. The relations between the various different approaches can advantageously be understood in the framework of intermediate state representations.[26] All these methods have in common that one starts from a closed-shell reference system and that the attachment spectrum is computed, that is, all attachment energies to the reference system are *directly* obtained from one calculation. In particular, a balanced description of the different attachment states is guaranteed to some order of perturbation theory. We have employed the EOM-CC method[25] implemented in the ACES II package,[27] and will present results for the two nitromethane anion states below.

Let us now turn to the cut through the surfaces that has been chosen along the straight line vector connecting the two minima $d = x^{DB} - x^V$ where x^{DB} and x^V represent the equilibrium structures of the dipole-bound and the valence states, respectively. A dimensionless 'reaction' coordinate s can then be defined *via* the geometrical structure

$$x(s) = x^{DB} + sd, \qquad (3.3)$$

that is, $s = 0$ and $s = 1$ correspond to the geometries of the dipole-bound and valence states, respectively.

The two equilibrium geometries x^{DB} and x^V have been computed at the coupled cluster with single and double substitutions (CCSD) level using Dunning's double-ζ basis[28] augmented with d-type polarisation (exponents 0.75, 0.8, and 0.85 on C, N, and O, respectively) and p-type diffuse functions (exponents 0.034, 0.048, and 0.059 on C, N, and O, respectively) on the heavy atoms (DZPD) as well as with a (11s4p)/[9s4p] set (X) to describe the dipole-bound electron. The X set was placed in a distance of 4 Å from the carbon atom in the direction of the dipole vector of the neutral

molecule (almost parallel to the CN bond) and consists of Dunning's double-ζ basis for hydrogen augmented with 7 even tempered s-type functions (exponents between 0.053 and 0.000039) and 4 even tempered p-type functions (exponents between 0.01 and 0.000156). Our CCSD/DZPD+X geometries are very similar to the results from ref. 9, and fall in fact between the CCSD(T)/6-311G++(2d2p) and HFDFT/6-311G++(2d2p) equilibrium structures given therein. Specifically, we find bond lengths that are somewhat longer (typically 0.007 Å) than the CCSD(T)/6-311G++(2d2p) values in ref. 9, and the respective values for the angles show differences of less than 0.3 degrees. Moreover, the adiabatic EA (AEA) of the valence state obtained from our CCSD/DZPD+X energies is −32 meV also in good agreement with the values from ref. 9 (note that the zero-point correction that stabilises the valence anion by roughly 70 meV is *not* included in our value).

Having established a cut through the two minima, we return to the computation of the two adiabatic states as a function of s. These calculations have been performed at the EOM-CC level of theory.[25] Three different basis sets have been used, the DZPD+X set described above, Dunning's augmented polarised valence double-ζ set (AUG-cc-pVDZ+X),[29] and Dunning's polarised valence triple-ζ set augmented with the s and p-type diffuse functions of the corresponding augmented set on the heavy atoms (cc-pVTZ+sp+X).[29] In comparison with separate CCSD calculations for the two anionic states, at the EOM-CC level one would expect the energy of the valence anion to be somewhat underestimated owing to the pronounced relaxation effects. This is indeed the case, as can be seen from the AEA listed in Table 1. For all three basis sets the EOM-CC AEAs are more negative by roughly 300 meV. Obviously, the EOM-CC description of the two anionic states is not perfectly balanced (assuming that it is reasonably well balanced in separate CCSD calculations). Nevertheless, keeping in mind that computing accurate EAs is notoriously difficult,[30,4] and that we are not so much interested in relative energies but rather in the avoided crossing structure, the EOM-CC results are quite satisfying.

The EOM-CC cuts through the two anionic PES are displayed in Fig. 2. Clearly, the results obtained with all three basis sets are qualitatively similar. On the lower adiabatic PES there is a small barrier separating the two minima which is obviously a manifestation of a relatively sharp avoided crossing with the second adiabatic state. As discussed above, close to the intersection of the anionic states, the higher state crosses also the neutral PES, and the 'last' *ab initio* points on our upper curves correspond to attachment energies of less than 0.1 meV (*cf.* the attachment energy of the dipole-bound electron that is in the order of 10 meV). In other words, in going from the 'last' point to slightly smaller s values the upper state is turned into a resonance, and to follow this curve one needs a method that takes electron autodetachment explicitly into account (see section 4). In this context we note

Table 1 Adiabatic electron affinities at different levels of theory. At the ΔCCSD levels the AEA is obtained from substracting the CCSD energies of the neutral and the valence anion at their respective equilibrium structures. In contrast, at the EOM-CC level the vertical electron attachment energy of the anion is computed directly which is then added to the energy it takes to 'deform' the neutral to the anionic structure. CCSD/DZPD+X geometries have been used, and zero point corrections are *not* included. All values are given in meV

	ΔCCSD	EOM-CC
DZPD+X	−32	−270
AUG-cc-pVDZ+X	130	−190
cc-pVTZ+sp+X	68	−200
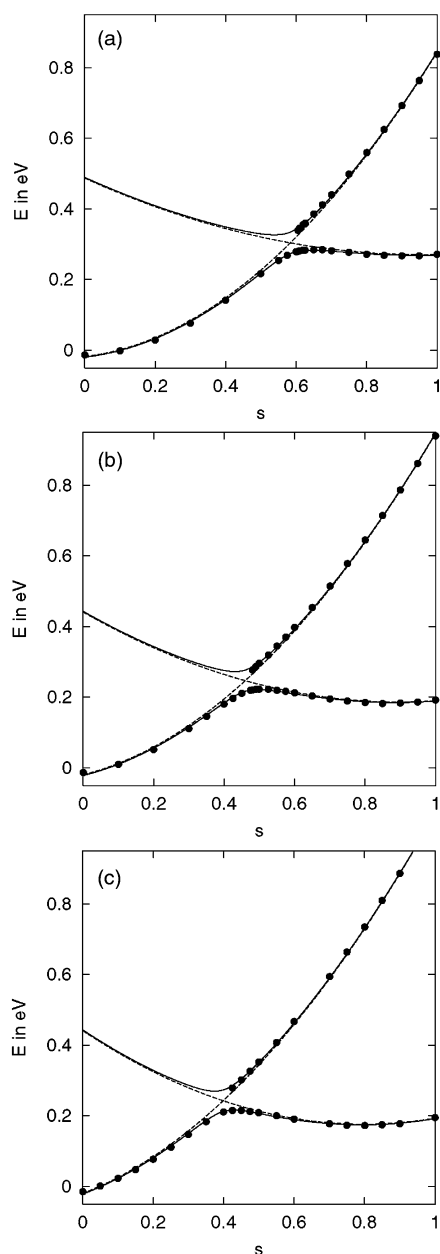
Fig. 2 Adiabatic and diabatic surfaces based on the EOM-CC *ab initio* data. The full circles represent the *ab initio* points of the adiabatic PES. The corresponding adiabatic and diabatic surfaces obtained from the least square fit of the model potential V to these data (*cf.* Table 2) are indicated as continuous and dashed lines, respectively. Upper panel: DZPD+X basis, medium panel: Aug-cc-pVDZ+X basis, lower panel: cc-pVTZ+sp+X basis set.

Table 2 Fitted parameters of the avoided crossing potential V defined in eqn. (2.1). The seven parameters have been obtained from a least square fit to the two adiabatic surfaces that have been computed at the EOM-CC level using the indicated basis sets. ω_1 and ω_2 are given in Hartrees, v_1, v_2 and W are given in meV. N is the number of *ab initio* energies used for the fit and χ^2 is the usual sum of squared data-point/model deviations in Hartrees

	DZPD+X	AUG-cc-pVDZ+X	cc-pVTZ+sp+X
ω_1	0.234	0.229	0.226
ω_2	0.131	0.153	0.175
s_1	-0.0790	-0.175	-0.275
s_2	0.963	0.896	0.798
v_1	-22	-41	-72
v_2	270	187	176
W	30.4	30.0	30.5
N	35	39	33
χ^2	$4.7 \cdot 10^{-7}$	$6.9 \cdot 10^{-7}$	$5.0 \cdot 10^{-7}$

extent on the basis set. In contrast, the off diagonal coupling term W is almost basis set independent, and we find a value of $W = 30$ meV (242 cm^{-1}). Let us note that owing to the 'local' symmetry of the NO$_2$ group, one could argue for an s-dependent coupling that should become very small – though not exactly zero – for a vanishing tilting angle of the NO$_2$ group. We have investigated fitting to $W' = \lambda s$ and to $W'' = W_0 + \lambda s$, but, with neither choice was the quality of the fit significantly improved. At least for fitting purposes only the value of W close to the intersection matters.

Our value for the coupling element W represents the first quantitative information on the coupling between a dipole-bound and a valence anion. The magnitude of W should be compared with the splitting of the adiabatic surfaces at the respective equilibrium structures which is much larger (≈ 1 eV). Thus, for the nitromethane anion we clearly have a weak coupling situation, and transitions from one anionic state to the other need to be discussed in terms of diabatic states, whereas an adiabatic barrier crossing picture is not appropriate. Some implications for the interpretation of experiments are pointed out in section 5.

4 Temporary nitromethane anion

We now turn to the second major obstacle for computing the two anionic PES: the valence state is a resonance in a considerable fraction of the relevant nuclear coordinate space. In this connection we also discuss the question of balanced MRCI expansions for the two nitromethane anion states.

In general, a resonance or temporary state is a state of a system that has sufficient energy to decay into one or more subsystems, and in the present context the relevant decay channel is electron autodetachment. Resonance states can be characterised by complex Siegert energies[31,32]

$$E_{\text{res}} = E_{\text{r}} - \text{i}(\Gamma/2), \qquad (4.4)$$

where E_{r} is the resonance energy or position usually measured with respect to the target in a scattering experiment, and Γ is the resonance width that is related to the lifetime $\tau = \hbar/\Gamma$. One possibility to compute complex resonance energies is to employ complex absorbing potentials (CAP),[33,34] and we have investigated the valence state at the geometry of neutral nitromethane using the CAP/CI method.[35] This method is particular attractive in the present context, since it can be combined with existing electron structure codes in a straightforward manner[35] and electron correlation effects can be incorporated efficiently.[36]

that owing to the X set, in our calculation there is a dense pseudo-continuum at low energies that immediately 'dissolves' the upper state as it crosses the neutral PES. Only for s values considerably below the point of intersection one can identify a state possessing mainly valence character in the EOM-CC calculations. Yet, the associated energies do not form a smooth curve, since the mixing with the pseudo-continuum states is obviously strongly s-dependent.

The parameters obtained from the least squares fit of the avoided crossing model potential V to the *ab initio* data are collected in Table 2. The overall quality of the fit (χ^2) is reasonably good, but small deviations between the *ab initio* and the model curves can be seen even on the coarse scale of Fig. 2. As expected, the parameters defining the harmonic diagonal terms, *i.e.*, the diabatic potentials, depend to a considerable

Independent of the particular method employed to treat the metastable state, a crucial point pertains to balancing the anion and the neutral-plus-free-electron aspects in the wavefunction (see *e.g.* ref. 35, 37, 38]). One usually distinguishes three levels of approximation, the static exchange (SE), the static exchange polarisation (SEP), and the MRCI level. At the SE level only configurations of the type (target)$^N(\phi^*)^1$ are taken into account, where (target) refers to the occupied SCF orbitals of the neutral target molecule possessing N electrons, and ϕ^* is a virtual orbital of appropriate symmetry. At the SEP level target polarisation, *i.e.*, orbital relaxation effects are included by adding all single excitations from the target orbitals, and at the MRCI level dynamic electron correlation is taken into account by building the CI space from all single and double excitations with respect to any of the SE configurations. From a viewpoint of balance, the energy as well as the lifetime of the temporary state are considerably overestimated at the SE level, somewhat underestimated at the SEP level, and only at the MRCI level a reasonably balanced description is achieved (see *e.g.* ref. 35, 38). These ideas can be borrowed to address the closely related problem of balancing valence and dipole bound states. In this context the SE level is obviously useless, and one needs to include at least the relaxation effects at a SEP-like level. Unfortunately, for nitromethane the SEP-analogue level is also not of much use, since the stability of valence state is too strongly overestimated (see below). Thus, one needs to go to the MRCI level, yet, the associated configuration space gets extremely large (*cf.* Table 3), and for nitromethane this level is for all but the smallest basis sets impractical.

A thorough description of the CAP/CI method has been given in ref. 39, and here we present only the details pertaining to the present calculations. The underlying one-particle basis set is Dunning's double-ζ (DZ) basis[28] augmented with a [6p]/(5p) set of diffuse functions at the nitrogen and oxygen atoms (even scaled exponents starting with half of the smallest p-exponent of the respective DZ set and using a scaling factor of 1.6). We were confined to this small basis set, since owing to the low symmetry of the system the MRCI configuration space gets large (Table 3), and presently, calculations with larger basis sets are too time consuming for us (note that in CAP/CI calculation several (here 15) eigenvectors of the CI matrix are needed). The dimension of the CI matrix was reduced *via* an energy selection scheme where those configurations are discarded whose perturbatively estimated contribution to the total energy is below a given threshold T.[40,41] For a discussion of this technique in the context of resonance states see ref. 36. The Hamilton and the CAP matrix have been computed using the MOLCAS[42] and the DIESELCI[43] packages of programs, and the eigenstates of the CAP/CI Hamiltonian have been computed using a Davidson algorithm adopted for complex-symmetric matrices.[44]

A rough estimate of the Siegert energy of the $^2A'$ $CH_3NO_2^-$ resonance state has been obtained at the SE level where we find a position of $E_r = 2.03$ eV and a width of $\Gamma = 0.46$ eV. As discussed above, these values can be viewed as generous 'upper bounds' for the resonance parameters. Going to the SEP level, the stability of the anionic valence state is greatly overestimated, and in fact, a bound valence state is predicted. Thus, no information about the resonance energy of $CH_3NO_2^-$ can be obtained at the SEP level, and the MRCI level is needed. Our results obtained with different selection thresholds T are collected in Table 3. Clearly, the resonance parameters converge with decreasing T, and our best values are $E_r = 0.73$ eV and $\Gamma = 0.25$ eV corresponding to a lifetime of 2.6 fs. We conclude that at the geometry of neutral nitromethane the valence anion is a typical shape-type resonance, and our results should be seen as a reasonable estimate for the resonance position in an electron scattering experiment. Regarding the trends observed at different levels of theory $CH_3NO_2^-$ behaves similar to many other anions,[4,35] and thus, we expect that if higher correlation effects are included and larger basis sets are used, the anionic state is further stabilised in the sense that slightly lower resonance positions and widths are found. To our knowledge there are no electron scattering data for nitromethane we could compare with, but our resonance position is surprisingly close to the resonance position observed in dissociative attachment[15] which often reflect the positions obtained from electron scattering.

Clearly, using an MRCI approach it is in principle possible to describe both the dipole-bound and the (temporary) valence state in a balanced manner. Yet, our experience with the temporary $CH_3NO_2^-$ anion state shows that the corresponding CI matrices are huge even if only small basis sets are employed. For basis sets that include a reasonable number of polarisation functions as well as the set of functions needed to describe the dipole-bound electron, the MRCI approach is effectively impractical. Thus, for the time being we cannot include the part of the adiabatic PES where the second state is a resonance into our considerations. Let us note that it is by no means clear to what extent the coupling between the two anionic states will be influenced by the coupling to the autodetachment continuum, in particular in view of the fact that the crossing of the higher adiabatic state with the neutral PES is essentially at the same geometry as the avoided crossing between the two anionic states.

5 Summary and conclusions

We have studied the coupling between the dipole-bound and the valence state of the nitromethane anion by *ab initio* methods. Specifically, we have investigated the two lowest adiabatic states of the nitromethane anion along a cut including the two minima corresponding to the dipole-bound and the valence state. This one-dimensional perspective seems appropriate for nitromethane, since the relevant electronic states and vibrational modes are totally symmetric. From an electronic structure theory point of view, the key points are a balanced description of two very different electronic states and the possibility of electron autodetachment from the higher state in a considerable range of nuclear coordinate space. For example, at the geometry of the neutral the valence state is a short lived shape-type resonance, and we predict a lifetime of 2.6 fs. Yet, the computation of the autodetachment width is a demanding task, and we were limited to quite restricted basis sets. Thus, we focused on bound state methods, and the second adiabatic PES was consequently computed only at geometries where it lies below the PES of neutral nitromethane. To obtain a balanced description of the two anionic states, the EOM-CC method was employed in conjunction with different one-particle basis sets. As can be seen from the calculated AEA, even at this sophisticated level of theory the strong relaxation effects in the valence state are not fully accounted for, but we expect a

Table 3 Resonance position and width for vertical electron attachment into the lowest $^2A'$ valence state of nitromethane. The energies have been obtained using the CAP/CI method and the DZ + 5p one-particle basis set at the CCSD/DZPD + X equilibrium geometry. T is the threshold used in the energy selection procedure of the many-particle basis set and D_{CI} is the corresponding dimension of the CI matrix

T Hartrees	D_{CI} 10^6 CSFs	E_r eV	Γ eV
$3 \cdot 10^{-6}$	0.45	1.58	0.29
$1 \cdot 10^{-6}$	0.92	1.09	0.26
$3 \cdot 10^{-7}$	1.6	0.83	0.25
$1 \cdot 10^{-7}$	2.4	0.73	0.25

satisfying characterisation of the coupling between the two anionic states.

From the *ab initio* PES the coupling between the dipole-bound and valence states of $CH_3NO_2^-$ was extracted by a least square fit of a simple avoided crossing model potential. The coupling parameter W is remarkable robust with respect to the one-particle basis set employed in the electronic structure calculations, and shows a value of about 30 meV. Note that we cannot draw any conclusions regarding the dependence of W on the nuclear coordinates, and our value represents the coupling at the intersection. Our study provides the first reliable estimate for the coupling between a dipole-bound and a valence state. It can for instance be employed to set up Landau Zener type surface hopping models, and allows us to address a number of qualitative issues. Yet, more calculations are needed to clarify the role of autodetachment and to explore the multi-dimensional PES. It will be interesting to see, whether the magnitude of the nitromethane coupling element is typical for a larger class of systems.

Regarding the particular value of $W = 30$ meV, we conclude that W is small with respect to the vertical excitation energies of the anionic states that are in the order of 1 eV. Thus, the nitromethane anion is clearly in the weak coupling regime, and any description of transitions between the dipole-bound and the valence state should be based on the diabatic picture. On the other hand, W is large compared with the mass spectrometric timescale of many experiments.[5,10,16] In first order perturbation theory the corresponding transition rate is essentially W^2 times a Franck–Condon factor, and even with very unfavourable Franck–Condon factors rapid transition are expected on a μs or even ms timescale appropriate for mass spectrometry.

Thus, on a mass spectrometric timescale the dipole bound state is indeed a very efficient doorway for electron attachment. The valence state is quickly populated, and can then be stabilised by collisions with a third body. In this light the strongly enhanced valence attachment upon argon-solvation[10] is readily understood, since the vibrational excited valence state can dissipate its energy by argon evaporation. Yet, the coupling is of course not a one-way doorway, and it should be possible to populate the dipole-bound state by vibrational excitation of the valence anion. Indeed, vibrational excitation of valence anions produced by a supersonic source and subsequent field detachment may provide a pathway to accurately measure the AEA of nitromethane. In conclusion, a pure dipole-bound state of $CH_3NO_2^-$ cannot survive on a μs timescale, and all anionic states energetically above the dipole-bound minimum will possess a mixed character. Our results suggest that considerably faster techniques are needed to observe pure dipole-bound states of nitromethane.

Acknowledgement

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