Quantum dynamical study of low-energy photoelectron bands of 2-phenylethyl-*N,N*-dimethylamine[#]

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Abstract. The first three photoelectron bands of 2-phenylethyl-*N,N*-dimethylamine (PENNA) are investigated theoretically, paying particular attention to the vibrational structure and to possible nonadiabatic coupling effects. A substantial vibronic interaction is established between the first and second excited cationic states (corresponding to the second and third photoelectron bands). Their coupling to the cationic ground state is found to be rather weak. This is tentatively attributed to the well-known fact that the latter carries a hole at the amine site, while the former two have the electron removed from benzene-type orbitals. The interaction between the two excited cationic states is characterized by a ‘hidden’ or local symmetry at the phenyl moiety. Preliminary dynamic calculations with two interacting electronic states and four vibrational modes are reported. The computed spectra are compared to experimental results of Weinkauff *et al.*

Keywords. Potential energy surfaces; vibronic interactions; conical intersections; photoelectron spectra.

1. Introduction

Vibronic interactions, i.e., the coupling of different electronic states through the nuclear motion are nowadays known to be an ubiquitous phenomenon in molecular spectroscopy and dynamics. They can give rise to a symmetry-lowering in excited states compared to the ground state, to the excitation of non-totally symmetric modes (in even and odd vibrational quanta) and, most notably, to a failure of the familiar adiabatic or Born-Oppenheimer separation of electronic and nuclear motions. Conical intersections (CoIns) of potential energy surfaces (PESs) have emerged as the paradigm of the latter situation and are at the focus of contemporary, experimental and theoretical research.^{1,2}

To facilitate theoretical treatments of these phenomena, symmetry is often exploited, if present.^{3,4} This reduces not only the computational cost, but may also allow for a more transparent interpretation of the results. Similarly, for larger systems a considerable simplification would be obtained, if they could be reduced to a number of weakly coupled moieties and the vibronic interactions be reduced to each of them individually.

In the present work, we analyse one example of current interest, paying particular attention to these aspects. The system chosen, 2-phenylethyl-*N,N*-dimethylamine (PENNA; see figure 1 for a schematic representation) has been analysed experimentally in the context of local ionization and charge transfer,^{5,6} and their elucidation by Rydberg fingerprint spectroscopy has been demonstrated.⁷ Its radical cation features two charge sites, the amine and phenyl moieties, which can be specifically accessed by two-photon ionization techniques with suitable pulses. This gives rise, among others, to ultrafast charge migration processes.^{8,9} Of further interest is a broad and nearly structureless band in the two-photon ionization spectrum obtained with 266 nm pulses.⁷ This is a typical feature associated with strong nonadiabatic interactions and CoIns of the pertinent PESs, which raises the question of such couplings between states with different charge centres.

In this paper, we report results of a partly preliminary theoretical analysis of this system and elucidate some of its characteristic features. The pertinent PESs have been characterized by cuts along all normal coordinates of PENNA, and important ones have been identified. A model Hamiltonian has been constructed on the basis of these results and the photoelectron (PE) spectral intensity has been computed. Substantial interactions between the states deriving from phenyl ionization have been obtained, and their spectral implications been established. The results are compared to experimental recordings of Weinkauff *et al.*⁷

[#]Dedicated to Prof. N Sathyamurthy on his 60th birthday

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2. Computational details

2.1 Vibronic coupling model

We seek to analyse the vibrational excitation and vibronic interactions occurring in the radical cation of PENNA within the multimode vibronic coupling (MMVC) model.^{3,4} Here, a diabatic electronic basis is employed and the resulting potential energy matrix expanded in a Taylor series in suitable normal coordinates Q_i

$$\mathbf{H} = (T_N + V_0) \mathbf{1} + \mathbf{W} \quad (1a)$$

$$T_N = -1/2 \sum \omega_i \delta^2 / \delta Q_i^2 \quad (1b)$$

$$V_0 = 1/2 \sum \omega_i Q_i^2 \quad (1c)$$

$$W_{\alpha\alpha} = E_\alpha + \sum k_i^{(\alpha)} Q_i + \sum g_{ii}^{(\alpha)} Q_i^2 \quad (1d)$$

$$W_{\alpha\beta} = \sum \lambda_j^{(\alpha\beta)} Q_j \quad (1e)$$

Here, the matrix elements refer to all the electronic states of the interacting manifold, namely the three lowest doublet states of the PENNA radical cation. $\mathbf{1}$ denotes the unit matrix in this function space. T_N stands for the nuclear kinetic energy and V_0 for the potential energy of the initial state which is taken to be the S_1 state of PENNA according to the experimental setup of Weinkauff *et al.*^{6,7} (For both operators the usual harmonic form is adopted). The first-order coupling constants $k_i^{(\alpha)}$ and $\lambda_j^{(\alpha\beta)}$ and the second-order coupling constants $g_{ii}^{(\alpha)}$ are to be determined by requiring that the model PESs of the Hamiltonian reproduce the potential energy data from *ab initio* calculations as closely as possible (e.g. by a least-squares fit). For displacement along a single mode Q_i this implies a parabolic form according to

$$V_\alpha(Q_i) = E_\alpha + \left(\omega_i/2 + g_{ii}^{(\alpha)} \right) Q_i^2 + k_i^{(\alpha)} Q_i, \quad (2)$$

while for a single mode Q_j the PECs read as

$$V_\pm(Q_j) = (E_\alpha + E_\beta)/2 + \omega_j Q_j^2/2 \pm \left[(E_\alpha - E_\beta)^2/4 + \lambda_j^2 Q_j^2 \right]^{1/2}, \quad (3)$$

that is, a superposition of parabolic plus hyperbolic terms. Since the specific procedures for the determination of the parameters, as well as all other aspects related to the Hamiltonian, have been amply described in the literature,^{3,4} we do not go into more details here.

2.2 Electronic structure and vibronic calculations

To get insight into the structural features of the system and determine the coupling constants mentioned in

the last paragraph, *ab initio* electronic structure calculations have been performed. As a starting point, the equilibrium geometry and normal coordinates in the S_0 and S_1 states of PENNA have been determined at the MP2 and CIS levels, respectively, using the cc-pVDZ basis set of Dunning.¹⁰ The results for the S_0 state agree generally well with the literature data.⁵ Those for the S_1 state are close to the results for the S_0 state which leads us to believe that the CIS results are trustworthy also there. (Higher-level calculations like the CISD method turned out to be too expensive for the present investigation). In the following, important step, ionic potential energy curves (PECs) along the S_1 normal coordinates are generated by computing S_0 ionization potentials for a set of suitable displacements (along the S_1 normal coordinates!) with the outer-valence Green's function method (OVGF, same basis set) and adding S_0 potential energies for each of these points using the MP2 method. This amounts to a simple computational scheme, including electron correlation, which allows for overview scans of the ionic PECs along all the potentially important normal coordinates of PENNA. Only the high-frequency hydrogen-stretching modes (numbered 58–72) are expected to have negligible influence and are dropped from the calculations (and subsequent considerations).

Given that the parameters entering the Hamiltonian are determined, the vibronic secular problem thus defined is solved by setting up the secular matrix in a direct product basis of harmonic oscillator basis functions pertinent to the operator $T_N + V_0$. It is diagonalized with the aid of the Lanczos algorithm.¹¹ The vibronic calculations all rely on the Heidelberg MCTDH program package,¹² while the electronic structure calculations have been performed using the Gaussian set of programs.¹³

3. Results and discussion

As stated above, in the first step the equilibrium geometries and vibrational frequencies of PENNA in its S_0 and S_1 electronic states have been determined. Various S_0 conformers have been identified, which are all similar to the results of reference 5, and the asymmetric anti conformer been verified as the global minimum (structure IV of reference 5, for a schematic drawing see figure 1). The structural parameters of the S_1 minimum are found to be quite similar, with maximum deviations from the S_0 minimum being 0.05 Å for the bond lengths and 1.5° for the bond angles. Correspondingly, the energy of the S_0 state at this geometry is only ~0.1 eV above its energetic minimum. The latter is

Figure 1. Schematic representation of PENNA. The black balls denote carbon atoms, blue stands for nitrogen and white for hydrogen.

taken as the zero of energy for all following data. The vertical (adiabatic) S_1 excitation energy is computed to be 6.14 eV (5.93 eV). The latter datum considerably exceeds the experimental result (4.66 eV) of reference 6.

3.1 Vertical ionization potentials and cationic potential energy surfaces

The aforementioned S_0 and S_1 stationary points have all been characterized as true local minima, with no imaginary frequencies. Subsequently, vertical ionization potentials (IPs) have been computed for the two local minima and by displacing the system along all normal coordinates of both the S_0 and S_1 normal modes (excepting only the C–H stretching modes). This amounts to 114 vibrational modes, with displacements ± 1 , ± 2 and ± 3 chosen for computing the IPs. Ionic potential energy curves for the three lowest electronic states of the radical cation have been constructed by adding the S_0 potential energy at these points.

The results for the vertical ionization potentials are depicted in graphical form in figure 2 which displays, apart from the energy data, also the underlying molecular orbitals out of which ionization takes place. As is well known,^{5–8} these reside on either the phenyl or the amine moiety. The HOMO and HOMO-1 (orbitals 40 and 41) are located on the phenyl side; however, due to electron correlation and reorganization effects,⁸ the lowest cationic state carries the charge at the amine site^{5–8} and corresponds to ionization out of HOMO-2 (orbital 39).⁸ This energetic re-ordering obtained by the elaborate ADC Green's function scheme⁸ is correctly described by the present OVGf calculation (see figure 2), which constitutes an important test of

Figure 2. Computed vertical ionization spectrum of PENNA (OVGF method) along with a schematic representation of the molecular orbitals from which ionization occurs.

our computational scheme. Further, the separation in space of the two charge centres will play a role in the subsequent discussion.

The ionic potential energy curves for the two sets of normal coordinates turn out to be rather similar, which is not surprising because of the similar S_0 and S_1 equilibrium structures. Further, we focus on the S_1 normal coordinates because the ‘initial’ state in the ionization process is the S_1 state according to the experimental setup of Weinkauff *et al.*⁷ For most coordinate directions the potential curves for the three ionic states are found to be nearly parallel to those of the S_1 state and, hence, no substantial vibrational excitation and neither vibronic interaction between them is expected. Notable exceptions are provided by modes 15, 17, 36 and 55, with potential energy curves for the three lowest ionic states as given in figure 3. In these cuts, the other normal coordinates are always chosen to be zero, and the origin thus denotes the centre of the FC zone, that is, the equilibrium geometry of the S_1 state.

Except for mode 55, three potential energy curves are given, as computed by the OVGf method. Their colours follow the same coding as the vertical IPs of figure 2, that is, the lowest curve (online blue) has the hole at the amine site, the higher-energy curves (red and green online) correspond to the hole at the phenyl moiety. For mode 55, only two curves are included, as computed using Koopmans’ theorem, and exhibit a symmetric behaviour with a double minimum shape of the lower curve. The computed data points (individual symbols) in all cases are well fit by the eigenvalues of the coupling model, equation (1) with only a κ term [modes 15, 17 and 36, equation (2)] or only a λ (off-diagonal) coupling term [mode 55, equation (3)].

Figure 3. Cuts through of the PESs of the three lowest electronic states of the PENNA radical cation. The normal coordinates selected are indicated below the abscissa axes. All other coordinates are put to zero. Note that mostly OVGf results are displayed, except for mode 55 which shows those obtained by applying Koopmans' theorem (the OVGf renormalization is subject to 'noninteracting' energy shifts¹⁴ and cannot describe the situation). The third cationic state does not interact with the two states shown and its PES is omitted for clarity in this panel.

Within the LVC coupling model, the former corresponds to totally symmetric modes characterized by shifted parabolas as PECs, the latter to non-totally symmetric modes with PECs amounting to a superposition of a parabolic and hyperbolic form.^{3,4} According to the good fit achieved, this seems an appropriate characterization also of PENNA, although (remarkably) this molecular system has no geometric symmetry elements, i.e., the point group is C_1 . We interpret this finding in terms of a (approximate or hidden) 'local' symmetry at the phenyl moiety. The HOMO and HOMO-1 of

figure 2 resemble closely the components of the doubly degenerate HOMO of isolated benzene; also the vibrational modes 36 and 55, depicted in figure 4, mostly involve the phenyl site and are similar to vibrational modes of benzene. Further evidence comes from the PECs along modes 11, 12, and 37 (not shown in the figures): they display a 'crossing' of the ground and first excited ionic states at least within the energy resolution of the calculation (estimated ~ 0.02 – 0.05 eV). This 'crossing' should be a weakly avoided crossing since the states do have the same symmetry; the weak

Figure 4. Schematic drawing of the normal coordinates of the relevant vibrational modes of PENNA (S_1). The displacement vectors denote (from left to right) Q_{15} , Q_{17} , Q_{36} and Q_{55} .

Table 1. Vertical ionization potentials, harmonic vibrational frequencies and linear coupling constants of the relevant D0 – D2 cationic states and vibrational modes of PENNA.

[eV]	ω (S1)	k (D1)	k (D2)	k (D0)
IP	–	8.5490	8.8730	8.3410
Mode 15	0.0678	–0.0167	0.0578	–0.0472
Mode 17	0.0747	–0.0346	0.0620	0.0133
Mode 36	0.1559	0.0715	–0.0775	0.0144
Mode 55	0.2077	$\lambda^{(1,2)} = 0.1862$		

interaction is attributed to the spatial separation of the different charge centres associated with the two states (amine and phenyl, see figure 2). This interesting finding deserves further analysis which is, however, beyond the scope of the present work.

The coupling constants and vibrational frequencies extracted from the aforementioned fits, represented by the full lines in figure 3, are collected in table 1. We reiterate, that the other vibrational modes not mentioned explicitly above, display approximately harmonic PECs, nearly parallel to the S_1 state, for the same displacements up to ± 3 .

3.2 Vibrational structure of photoelectron spectrum

In the following we investigate the impact of the above PECs and coupling elements on the photoelectron spectrum of PENNA. The vibronic Hamiltonian is defined by equation (1) and the parameters of table 1. As already indicated, the interaction between the different charge sites (ground and first two excited cationic states, respectively) is found to be weak and neglected. We are thus dealing with two (excited) interacting states and four vibrational modes. The resulting vibronic line spectra for the first and the second excited state of the

Figure 5. Theoretical PE spectrum for PENNA after ionization from the S_1 state. The line spectra, obtained with the parameters of table 1, are to be convoluted, e.g., with a Lorentzian of suitable width to account for finite experimental resolution and other broadening effects. Left panels: PE band for transition to the D1 (first excited) state. Right panels: PE band for transition to the D2 (second excited) state. Upper row: coupling between D1 and D2 states included. Lower row: spectra without inter-state D1-D2 coupling.

PENNA radical cation all shown separately in the left and right panels of figure 5, respectively. The upper row of the panels display the results with the interstate coupling $\sim \lambda^{(1,2)}$ included, while in the lower two panels it is suppressed. An irregular, moderately dense line spectrum is discerned in the upper right panel while the upper left one displays only weak vibrational excitation. The irregularity is less pronounced than in other cases of conically intersecting PESs.¹ It should be pointed out, that the PECs of figure 3 indeed imply conical intersections here. However, the interacting electronic states are rather close in energy and the number of non-separable vibrational modes is moderate only, so that the density of vibronic levels is rather sparse, which is reflected in the spectral line structure. The lower two panels show only the excitation of the ‘tuning’ modes 15, 17 and 36 according to the Poisson intensity distribution formula.^{3,4} For the D2 state, fundamentals of modes 15 and 17 are observed near 8.88 eV; for the D1 state weak fundamentals are found near 8.6 eV and 8.68 eV and assigned to modes 17 and 36 [see also table 1 and the ensuing ratios $(k/\omega)^2$]. When comparing upper and lower panels one sees that the D1 state spectral profile is hardly affected by the interstate coupling, while for the D2 state this leads to a marked redistribution of spectral intensity (as is usual for the higher-energy partner of the interacting states).^{3,4}

To compare with experiment, it has to be born in mind that the initial electronic state is the S_1 state which involves electronic excitation at the phenyl site.⁷ This raises the question of the purely electronic ionization probabilities which determine the relative weights of how to superimpose the spectral bands of figure 5. For the same reason, ionization at the amine site is not expected to occur, or occurs with only very small probability (which is one reason why this band has not been included in the figure). The experimental spectral profile⁷ is characterized by a very broad distribution leading to a gradual and monotonous intensity decrease from the energy range of the (intense) phenyl ionization (around 9 eV) to that of amine ionization (near 7.5 eV), where the spectral intensity goes to zero. This feature is apparently not recovered in the present calculation, one further reason being the rather high first IP of 8.35 eV obtained here. An improved treatment of electron correlation and relaxation effects lowers this number to slightly below 8 eV.⁸ Also, as indicated above, the present calculation gives only a weak interaction between the two charge centres (neglected in the spectral simulations). This remains to be investigated by more sophisticated electronic structure calculations. On the other hand, it should also be born in mind that other possible mechanisms for the broad and structure-

less band are conceivable and have been discussed in reference 7. More work is needed to arrive at a better understanding of this intriguing phenomenon.

4. Summary and conclusions

In the present work we have theoretically studied the photoionization of PENNA through prior excitation of the S_1 state, localized at the phenyl site. As argued earlier, the occurrence of two charge centres (phenyl and amine) gives rise to special phenomena like local ionization and charge transfer, which have been explored both experimentally and theoretically.⁶⁻⁸ In the present contribution we have focused on the vibrational excitation and vibronic interactions accompanying the ionization process. Extensive calculations along all vibrational modes have been performed and the S_0 and S_1 normal coordinates have been compared. The effects of geometry changes have been found to be moderate and have been traced to a rather small number of vibrational modes. The analysis of the vibronic interactions points toward the (possibly) weak interactions between the charge centres. This may be the reason for the weak vibronic interactions between the ground and excited ionic states, and also for the existence of a ‘hidden’ or ‘local’ (approximate) symmetry at the phenyl site, leading to the characteristic PECs of figure 3. As a word of caution, in this first, partly exploratory, study a compromise has been made between accuracy and feasibility of the *ab initio* computations. More elaborate electronic structure schemes are available which can be employed, guided by the present results. This is planned for subsequent work, and will shed further light on the dynamics in this type of compounds.

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