Resonances in molecules and molecular clusters

Journal Item

Resonances in molecules and molecular clusters

Resonances in molecules and molecular clusters

Jimena D Gorfinkiel

School of Physical Sciences, The Open University, Milton Keynes, MK7 6AA, UK

E-mail: J.Gorfinkiel@open.ac.uk

Abstract. Resonances play an important role in a number of atomic and molecular processes. Identifying and characterising resonances in electron scattering is essential as they can both enhance a number of processes (e.g. electronic and vibrational excitation) and are crucial in others like dissociative electron attachment and dissociative recombination. We discuss recent theoretical studies of shape and core-excited resonances, both in isolated molecules of biological relevance and in small molecular clusters. The latter are investigated to understand the effect of the environment, in particular hydration, in electron collisions in biological matter.

1. Introduction

Temporary anion states (also known as resonances) can enhance most electron-induced processes. More interestingly, they can be chemistry initiators by leading to the break-up of the molecule into at least one reactive species. Resonances are also important in other molecular processes, for example, photodetachment and associative detachment. Theoretical research on their identification and characterization is therefore an active area particularly, but not uniquely, associated to the understanding of electron-induced processes in molecules. Besides their fundamental interest, resonance mediated or enhanced processes are relevant in a number of applied fields, from the modelling of radiation for medical uses to focused electron beam induced deposition and nanofabrication [1].

Scattering methods are an effective tool for the accurate description of resonances [1]: the modelling of shape resonances can be done using several of these approaches, both for small and larger molecules. Core-excited resonances are harder to model accurately, because of the importance of correlation in their description. However, both types of resonances (and vibrational Feshbach resonances) play an important role in, among others, biological radiation induced damage and electron transfer reactions.

Recent joint theoretical and experimental work on pyrimidine [2] and thiophene [3] using electron energy loss spectroscopy [4] and the R-matrix method [5] has confirmed the ability of this theoretical approach to accurately describe core-excited resonances in mid-size molecules in the gas phase.

Nonetheless, a lot of the scattering processes of applied relevance happen in a condensed environment, where the target molecule is surrounded by other molecules. In particular, in cellular environments, biomolecules (DNA, proteins, etc.) are surrounded by water. To bridge the gap between our understanding of resonance formation in molecules in the gas phase and that in a condensed environment, molecular clusters are being investigated, both theoretically and experimentally [6].

Here, we briefly describe results obtained with the R-matrix method both for isolated molecules (pyrimidine) and small molecular clusters.

2. R-matrix method

The R-matrix method [5] is based on the separation of space into an inner region, containing the electronic density of all the target (molecule or cluster) electronic states of interest and an outer region where the scattering electron is distinguishable from the bound electrons. A sphere of radius a, known as the R-matrix sphere, separates both regions.

In the inner region, an accurate description of exchange and correlation is necessary and the wave functions describing the N+1-electron system (N-electron target + scattering electron) can be written as:

$$\Psi_k^{N+1} = \mathcal{A} \sum_{i=1}^{n} \sum_{j=1}^{n_c} \Phi_i(\mathbf{x}_N; \hat{r}_{N+1}; \sigma_{N+1}) \frac{u_{ij}(r_{N+1})}{r_{N+1}} a_{ijk} + \sum_{i=1}^{m} \chi_i(\mathbf{x}_{N+1}) b_{ik} \tag{1}$$

where $\mathbf{x}_N$ and $\mathbf{x}_{N+1}$ stand for the spin-space coordinates of all N/N+1 electrons, respectively. r_{N+1} and $\hat{\mathrm{r}}_{N+1}$ correspond to the radial and angular coordinates of the scattering electron respectively and σ_{N+1} stands for its spin. The wave function Φ_i describes the ith electronic state of the target, as well as the angular and spin behaviour of the scattering electron. The functions $\frac{u_{ij}(r_{N+1})}{r_{N+1}}$ describe the radial behaviour of the scattering electron while the L^2-integrable functions χ_i are crucial for a good description of the short-range polarisation-correlation effects. $\mathcal{A}$ is the antisymmetrization operator, and the coefficients a_{ijk} and b_{ik} are determined by the requirement that the functions Ψ_k^{N+1} diagonalise the N+1 non-relativistic Hermitian Hamiltonian in the inner region [5].

In the outer region, the interaction between the scattering electron and the target molecule can be described using a single-centre multipole potential expansion. The basis functions Ψ_k^{N+1} and their associated eigenvalues are used to construct the R-matrix at the boundary between the regions. This R-matrix is propagated to an asymptotic distance where, by matching with known asymptotic expressions, the K-matrix can be determined. Resonance energies and lifetimes can then be obtained in several ways, in particular: (i) by fitting the eigenphase sum, $\delta_{sum}(E)$, obtained from diagonalizing the K-matrix using the well known Breit-Wigner expression:

$$\delta_{sum}(E) = \delta_r + \delta_{bg} = -\arctan \frac{\Gamma/2}{E - E_r} + \delta_{bg} \tag{2}$$

where E_r and Γ are the energy and width of the resonance respectively (and therefore its lifetime is $\tau = 1/\Gamma$); (ii) by calculating the S-matrices and, from them, the time-delay matrices:

$$\mathbf{Q}(E) = i\hbar \mathbf{S} \frac{d\mathbf{S}}{dE} \tag{3}$$

Peaks in the largest eigenvalues of $\mathbf{Q}(E)$ can be fitted to Lorentzian functions that depend on the resonance energy and width thus enabling their determination.

3. Results

Use of the R-matrix method and the UKRmol/UKRmol+ [7, 8] suites has enabled the investigation of shape and core-excited resonances in small and medium size molecules as well as the study of shape resonances in molecular clusters.

Below, we show two illustrative examples: pyrimidine, in which most core-excited resonances identified have been confirmed experimentally and thymine-$(H_2O)_5$ clusters, in which we have investigated the properties of hydration effects on resonance formation.

3.1. Core-excited resonances in pyrimidine

The nucleobases are one of the DNA constituents more widely studied, both experimentally and theoretically [9, 6]. However, whereas several works measured the anion yields due to dissociative electron attachment (DEA) both in the lower energy range, where shape resonances are responsible for the DEA, and at higher-energies, where core-excited resonances play an important role, not a lot is known about these core-excited resonances. The R-matrix approach has been applied to their study in both pyrimidinic and purinic DNA bases [10, 11, 12, 13] and (some of) the core-excited resonances of uracil have been investigated with other methodologies [14]. However, due to the lack of experimental information on the resonances themselves and the difficulty of linking one in a usually fairly dense spectrum of resonances with specific DEA products, it is difficult to ascertain the accuracy of the computational results.

A more satisfactory situation is found for pyrimidine, a model for pyrimidinic nucleobases: electron energy loss (EEL) spectra of it are available and enable a comparison with sophisticated R-matrix calculations. The comparison [2] shows excellent agreement between the resonances described by the calculation and those visible in the EEL spectra, if one accounts for the shift to higher energies in the computational results. This shift is due to an incomplete representation of the polarization effects in the R-matrix close-coupling calculations: for highly polarizable molecules (the spherical polarizability of pyrimidine is over 60 a_0^3) the standard close-coupling expansion is insufficient to fully describe the polarizing effect of the scattering electron. The amount of polarization described can not be quantified in this approach, but a qualitative indication of how well it is described can be obtained from comparing calculated shape resonance positions to experimental values. Use of pseudostates is likely to resolve the problem of underrepresentation [15, 16] but, until very recent software developments [8], the size of the calculations made them unfeasible.

Of all the resonances identified and characterized in the R-matrix calculations, 9 manifest themselves in the cross sections for exciting those states of pyrimidine that contribute to the energy losses ΔE=4.26 eV and ΔE=5.2 eV for which we have performed a comparison. Of these 9, two are not seen in the excitation cross sections, but the other 7 are; these results are summarized in table 1. The resonances that are not visible correspond to smaller peaks that would be 'washed out' in the experiment due to a broad Franck-Condon envelope. We note that these resonances, unlike all the others, are described by configurations in which an electron from a non-bonding orbital has been promoted to one of the lower π^* orbitals [2].

This kind of agreement between calculated and measured core-excited resonances has also been found for thiophene [3]: for this target, the cross sections for excitation into the first and second excited states calculated for two scattering angles (90° and 135°) agree very well with the EEL data and four core-excited resonances are clearly observed in both. These results demonstrate the capability of the R-matrix approach to model core-excited shape resonances in mid-size molecules of biological interest.

3.2. Effect of hydration

In order to understand the effect of hydration on resonance formation, we performed two sets of detailed investigations: ones for clusters of pyridine and another for thymine both with up to 5 water molecules. The aim was to gain insight into how the low energy π^* shape resonances in these molecules are affected by the presence of a few water molecules in their environment.

There were two main purposes of these studies: (i) to confirm, for larger molecules, the findings of Freitas *et al.* [18] in their study of HCOOH clusters with one and two water molecules; (ii) to extend the investigation to larger clusters. We note that whereas in the case of thymine additional water molecules will hydrogen-bond to the thymine itself, in the case of pyrimidine, these molecules hydrogen-bond to one another at the nitrogen 'end' of the molecule. This difference enabled us to investigate different effects [19, 20].

Table 1. Positions and calculated widths when available [17] (both in eV) of the core-excited resonances of pyrimidine identified in the calculations and the EEL spectra for Ranges I and II (see details in Regeta *et al.* [2]); note that the first resonance listed is actually of mixed shape and core-excited character.

Symmetry	Calculated		EEL
	E	Γ	
$^2B_1$	4.78	0.38	4.35
$^2A_1$	5.96	0.18	-
$^2A_1$	6.15	0.18	-
$^2A_2$	6.11	0.51	5.55
$^2B_1$	6.37	0.58	5.55
$^2B_1$	7.11	0.48	6.52
$^2A_2$	7.33	0.43	6.52
$^2B_1$	8.47	1.69	7.45
$^2B_1$	12.3	-	10.3

The calculations presented were performed at static-exchange level to avoid uncertainty in the relative description of polarization effects. Nonetheless, calculations were also performed at static-exchange plus polarization level and the results obtained were qualitatively the same. The cc-pVDZ basis set was used to generate Hartree-Fock orbitals; due to the size of some of the clusters, an R-matrix radius of 18 a_0 was necessary. The geometries of the thymine clusters investigated were obtained from that determined by Smyth *et al.* [21] for the thymine-$(H_2O)_5$ cluster using sophisticated DFT calculations.

We interpreted the effects of hydration as arising from two distinct contributions, that we labelled indirect and direct effects. The indirect effects are due to the *distortion of the molecular geometry* caused by the presence of the water molecules; the direct effect is that due to the *presence* of the water molecules itself. In other words: the indirect effect can be computed in calculations by investigating the molecule of interest isolated, first in its equilibrium geometry and then in the geometry it adopts in the cluster; the direct effect is computed by comparing the resonances of the isolated molecule *in the cluster geometry* and those in the clusters themselves. The total effect of hydration is the sum of these two effects. We note that the effects can both go in the same direction (e.g. both lowering the energy of the resonance or both raising it) or not. In addition, the direct and indirect effects, as well as the total effect depend (weakly, for these systems) on the site to which the water molecule attaches via hydrogen bonding.

Figure 1 shows the time-delay for isolated thymine together with that for 5 different thymine-H_2O clusters. The geometries of the clusters correspond to taking the lowest energy geometry of thymine-$(H_2O)_5$ in its electronic ground state (shown in figure 2) and removing four of the water molecules. Three well defined peaks are visible in the time-delay: the two lower ones (for all targets) correspond to the first and second π^* resonances of thymine, of pure shape character. The third one corresponds to the third π^* resonance, that is of mixed shape core-excited shape character (and, for this reason, given that our calculation does not describe inelastic channels, is excluded from the analysis).

Two of the dimers (A and D) involve water being the hydrogen acceptor in the bond: in agreement with Freitas *et al*'s conclusions, these lead to a 'destabilization' of the resonances, i.e. a shift to higher energies. Conversely, dimers B, C and E correspond to situations in which water is the hydrogen donor. In this case, the resonances are 'stabilized', i.e. shifted to lower energies.

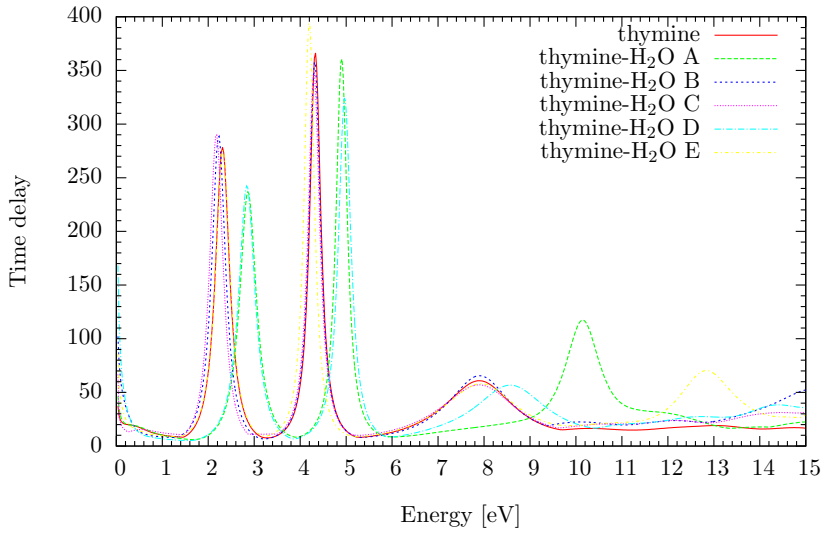

Figure 1. Largest eigenvalue of the time-delay matrix showing the first and second shape π^* resonances as well as the third mixed character π^* one in isolated thymine (red line) and 5 different thymine-H_2O clusters. The clusters are labelled according to which single H_2O molecule in the thymine-$(H_2O)_5$ cluster is taken into consideration. Note that the yellow line corresponding to cluster E is hardly visible under the red line and that the lines for clusters A and D overlap almost fully for the first two peaks.

The destabilizing shift is bigger than the stabilizing one. In addition, small differences can be observed between the resonance position for different geometries of the cluster corresponding to donor/acceptor situations: this shows that there is a (small) effect due to the specific site (atom) the water molecule binds to.

We have also observed that the effect of adding more water molecules, at least those that will form a hydrogen bond with the target of interest, is qualitatively additive; that is, it is possible (in general) to correctly predict whether resonances will be stabilized or destabilized but the shifts due to individual water molecules don't add up to the total shift. The prediction from figure 2 is therefore that the combined effect of the 5 water molecules would be small: the addition of two destabilizing water molecules and three stabilizing ones (whose effect is smaller), should lead to small shifts in the resonances towards lower energies. Indeed, the resonance shifts in thymine-$(H_2O)_5$ are 0.075 and 0.29 eV for the first and second π^* resonance respectively. Interestingly, the fact that one of the shifts is more than three times bigger than the other is not obvious from the shifts that occur when individual water molecules are present.

4. Conclusions

Theoretical and, more significantly, computational improvements over the last decades, have enable the accurate investigation of shape and core-excited resonances in molecules of biological relevance. Comparison with EEL spectra confirm that core-excited shape resonances in pyrimidine are well described when sophisticated models are used in R-matrix calculations. This paves the way for the study of DEA via these resonances, for which little is known beyond the measurement of anion production.

The effect of an aqueous environment on resonance formation and DEA can also be studied computationally, but in a less accurate manner. In this paper, we show that it is possible to calculate resonance positions (and widths) in an *ab initio* fashion and that the calculations enable

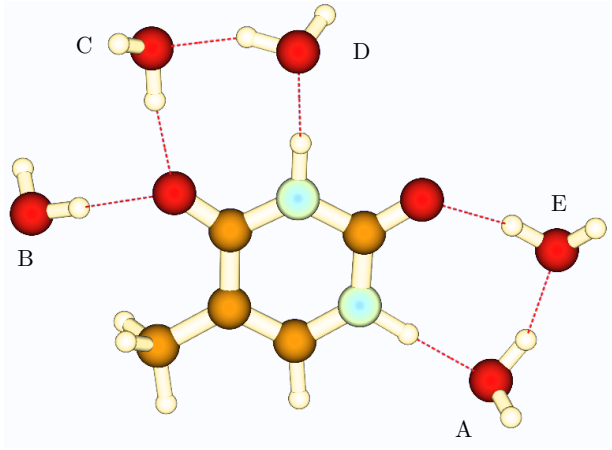

Figure 2. Lowest-energy geometry of the thymine-$(H_2O)_5$ cluster as determined by Smyth *et al.* [21]. The bottom right-hand molecule corresponds to 'A' and the labelling continues clockwise from it.

us to gain insight into the effect of hydrogen bonding on resonances. This insight could help us predict how resonances will be affected for systems for which calculations are still unfeasible.

Nonetheless, it is important to highlight that the microhydration effects on resonance formation do not provide the whole picture. Comparison with DEA experiments indicate that knowledge of the changes in resonance characteristics are not sufficient to provide even a correct qualitative picture of the effect on DEA. Recent experiments have shown this for the case of hydrogen loss from uracil and thymine in small clusters where experiments identified a complete quenching of this DEA channel at low energies upon hydration [22]. The calculations demonstrate that it is the presence of water that hinders H loss from hydrated nucleobases [23], and that this is not a resonance-related effect.

Acknowledgements

I gratefully acknowledge the contribution of many collaborators to the work presented in this paper, in particular Drs. Z. Mašín, A. Sieradzka, K. Regeta and Prof. M. Allan and Ms. Alexandra Loupas. This work used the ARCHER UK National Supercomputing Service (http://www.archer.ac.uk).

References

[1] Ingólfsson O 2019 *Low-Energy Electrons: Fundamentals and Applications* (Jenny Stanford Publishing)
[2] Regeta K, Allan M, Mašín Z and Gorfinkiel J D 2016 *J. Chem. Phys.* **144** 024302
[3] Loupas A, Regeta K, Allan M and Gorfinkiel J D 2018 *J. Phys. Chem.* A **122** 1146
[4] Regeta K and Allan M 2015 *Phys. Rev.* A **91** 012707
[5] Tennyson J 2010 *Phys. Rep.* **491** 29
[6] Gorfinkiel J D and Ptasińska S 2017 *J. Phys. B: At. Mol. Opt. Phys.* **50** 182001
[7] Carr J M, Galiatsatos P G, Gorfinkiel J D, Harvey A G, Lysaght M A, Madden D, Mašín Z, Plummer M, Tennyson J and Varambhia H N 2012 *Eur. Phys. J.* D **66** 20653
[8] Mašín Z, Benda J, Gorfinkiel J D, Harvey A G and Tennyson J *Comp. Phys. Commun.* submitted
[9] Baccarelli I, Bald I, Gianturco F A, Illenberger E and Kopyra J 2011 *Phys. Rep.* **508** 1
[10] Dora A, Tennyson J, Bryjko L and van Mourik T 2009 *J. Chem. Phys.* **130** 164307

[12] Dora A, Bryjko L, van Mourik T and Tennyson J 2012 *J. Phys. B: At. Mol. Opt. Phys.* **45** 175203
[13] Dora A, Bryjko L, van Mourik T and Tennyson J 2012 *J. Chem. Phys.* **136** 024324
[14] Fennimore M A and Matsika S 2016 *Phys. Chem. Chem. Phys.* **18**(44) 30536–30545
[15] Gorfinkiel J D and Tennyson J 2004 *J. Phys. B: At. Mol. Opt. Phys.* **37** L343
[16] Gorfinkiel J D and Tennyson J 2005 *J. Phys. B: At. Mol. Opt. Phys.* **38** 1607–1622
[17] Mašín Z and Gorfinkiel J D 2012 *J. Chem. Phys.* **137** 204312
[18] Freitas T C, Coutinho K, Varella M, Lima M A P and Canuto S 2013 *J. Chem. Phys.* **138**
[19] Sieradzka A and Gorfinkiel J D 2017 *J. Chem. Phys.* **147** 034302
[20] Sieradzka A and Gorfinkiel J D 2017 *J. Chem. Phys.* **147** 034303
[21] Smyth M, Kohanoff J and Fabrikant I I 2014 *J. Chem. Phys.* **140** 184313
[22] Kočišek J, Pysanenko A, Fárník M and Fedor J 2016 *J. Phys. Chem. Lett.* **7** 3401
[23] McAllister M, Kazemigazestane N, Henry L, Gu B, Fabrikant I, Tribello G and Kohanoff J 2019 *J. Phys. Chem.* B **123** 1537