THEORETICAL MODELLING OF JAHN-TELLER DISTORTED C60 ANIONS ON A SURFACE

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Abstract- Through the use of scanning tunnelling microscopy (STM), it is possible to directly observe the molecular orbitals associated with a particular molecule. For the charged ions of the C60 fullerene, the interpretation of these experimental images has an additional complication due to the inherent presence of the Jahn-Teller (JT) effect. In this work, the influence of the JT effect on STM images is examined. We also include interactions between the molecule and both the surface substrate on which it rests, and, when present within a monolayer, the nearest neighbours. Simple symmetry arguments are used to explain the effects of these external interactions on the energy of the different JT wells relating to molecular distortions of D3d, D5d, and D2h symmetry. We first investigate the C-60 monoanion, and then, through the construction of multi-electron states, move on to consider anions with higher charges. It is found that for high symmetry orientations of the molecule on the surface, the wells that are degenerate in the absence of external interactions split into equal energy subgroups, with the grouping dependent on the orientation of the molecule. H¨uckel molecular orbital theory is then used to investigate the effect this has on STM images. We show that when dynamic JT effects are considered, the images are always formed from some linear combination of the squares of the individual single electron molecular orbitals that make up the lowest unoccupied molecular orbital of the neutral molecule.

I. INTRODUCTION

Through the use of scanning tunnelling microscopy (STM), molecules which undergo a Jahn-Teller (JT) distortion can be directly imaged, providing useful information on the nature of the symmetry reduction this effect causes. The ions of the C60 fullerene molecule are ideal candidates for analysing this because the large size of the molecule makes it easily discernible via STM. High degeneracies in the electronic and vibrational states are lifted by the JT effect, producing splittings in the electronic states. A signature of this splitting is apparent in observed STM images.

For isolated anions of C60, the JT effect is expected to reduce the symmetry of the molecule from Ih to either D5d, D3d, D2h, or C2h [1, 2, 3], producing a selection of isoenergetic wells in the lowest adiabatic potential energy surface (APES). When quadratic JT effects are strong, the JT effect is static; the energy barrier between each of these wells is high, causing the system to become locked into a single distortion. The effect this would have on the STM images of the C□60 ion has been discussed previously [4]. Alternatively, if the quadratic JT effects are weaker, the JT effect will be dynamic. The energy barrier between minimum energy wells will be sufficiently small to allow the molecular distortion to pseudorotate between the equivalent lowest energy distortions. If the barriers in the APES are relatively high, the system is expected to spend negligible time in intermediate distorted configurations, and the distortion will 'hop' between wells. If the barrier is smaller, the time spent at intermediate positions will become significant giving a hindered pseudorotation. In the limit of a negligible barrier height, a free pseudorotation occurs, where equal time is spent in all possible distortions. It is expected that at realistic coupling strengths, the pseudorotation occurs on a timescale that is much quicker than that of STM measurements, and therefore all lowest energy distortions will be imaged simultaneously. In constructing STM images, we will use H¨uckel molecular orbital (HMO) theory, rather than the more commonly used density functional theory (DFT), due to its speed and simplicity. As _ orbitals contribute the overwhelming proportion of the bonding in C60, little error is introduced when constructing molecular orbitals by neglecting _ bonding, and it is this assumption that forms the basis of HMO theory. Indeed, there is excellent agreement between the molecular orbitals obtained for the neutral C60 molecule using both DFT and HMO theory [5, 6, 7, 8]. In this work, interactions between C60 ions and both the surface substrate and neighbouring ions will be treated using simple symmetry arguments to model the effect on the molecular distortion. The effect these interactions have on the C□60 anion will then be investigated, and a comparison made between the theoretical method and experimentally obtained images. We will then extend the method to the higher charged anions by constructing multi-electron states that are functions of the single electron orbitals that make up the lowest unoccupied molecular orbital (LUMO). A comparison will be made with experimental images of the unoccupied states of the C4□ 60 anion.

II. MODELLING THE JAHN-TELLER EFFECT AND EXTERNAL INTERACTIONS IN C¯60

We will assume that C60 molecules are adsorbed onto a surface, either as an isolated molecule or as part of a monolayer. In this section, we will consider

the case in which STM probes the states of the singly-charged anion, C□60. This could represent the case where C□60 ions are intrinsically present on a surface. Alternatively, the STM measurement process could result in the C□60 states being probed. A brief overview will be given of how the JT effect is modelled in the monoanion, and of the way in which an external interaction is treated. The two interactions will then be combined to see the effect of different molecular orientations on the surface adsorbed, JT-active anion.

2.1. Jahn-Teller interactions

The LUMO of C60 is three fold degenerate and is described by the T1u irrep. When the molecule is ionised to form C□60, the additional electron occupies this T1u state, and couples to eight hg modes to give a T1u8hg JT effect. Each mode will correspond to different nuclear displacements. However, these displacements are too small to be discernible in an STM experiment. As only the splitting of the electronic state is required, the only consideration is of what symmetry the molecule reduces to, and for this, a single effective mode can be considered. The JT interaction can be expressed by a linear coupling Hamiltonian and two (due to the non-simple reducibility of the H H product) quadratic coupling Hamiltonians. We will follow [1] and write the Hamiltonians using two-fold molecular axes fX; Y;Zg which align with double bonds of the molecule. When a C60 molecule is adsorbed on a surface, we will later also use axes fx; y; zg where z refers to the direction perpendicular to the surface. The full JT Hamiltonian can be written as:

$$H_{JT} = V_1 H_1 + V_2 H_2 + V_3 H_3 + \frac{1}{2}\mu\omega^2 \sum_{\gamma} Q_{\gamma}^2. \qquad (1)$$

Here, V1, V2 and V3 are the linear and two quadratic coupling constants respectively, _ is the mass and ! is the frequency of the (effective) hg mode, and sums over all 5 of the vibrational coordinates Qγ of the vibrational hg mode. These Qs are denoted fQθ;Qϵ;Q4;Q5;Q6g which transform according to the linear combination of the d-type orbitals

$$\{\sqrt{\frac{3}{8}}d_{3Z^2-R^2} + \sqrt{\frac{5}{8}}d_{X^2-Y^2}, \sqrt{\frac{3}{8}}d_{X^2-Y^2} - \sqrt{\frac{5}{8}}d_{3Z^2-R^2}, d_{YZ}, d_{ZX}, d_{XY}\}. \qquad (2)$$

The forms of the matrices representing these Hamiltonians can be found in ref. [1]. Diagonalising the Hamiltonian results in an energy expression that is a function of the coupling constants and the Qs. For given values of the coupling constants, the lowest energy eigenvalue can be minimised with respect to the Qs revealing the symmetry of the distorted molecule, which, for C□60 is predominantly to either D3d or D5d symmetry. Following the convention set out in ref. [1], the six D5d wells are labelled A to F and the ten D3d wells are labelled a to j. For some regions of coupling values it is also possible that the molecule distort to D2h symmetry, which has 15 wells which will be labelled A to O as in [4]. Distortion to C2h symmetry is also possible for a very small range of coupling constants, but this will not be considered in this paper.

2.2. External interactions

We will assume that the effect on a C60 molecule of interactions with a surface substrate is to perturb the atoms closest to the surface in some way such that the symmetry is reduced. For many common surfaces, such as Ag or Au, it will be appropriate to treat the surface as being homogeneous in the plane of the surface. The effect on the C60 molecule is therefore to remove the equivalence between the z axis (perpendicular to the surface) and the x and y axes (in the plane of the surface). For a C60 oriented with a pentagon prone to the surface, this can be visualised in terms of the symmetry reduction depicted in figure 1. The fivefold rotation about the (z) axis through the centre of the uppermost pentagon remains as a symmetry axis. However, fivefold rotations about axes through the centres of the other pentagons are no longer symmetry operations. Similarly, reflections in various vertical planes are allowed but not in other planes that would be equivalent in the undistorted molecule. In this case, the reduction in symmetry induced by adsorption on the surface is to the C5v point group. Similarly, when the molecule is adsorbed with a hexagon or double bond uppermost, the symmetry is reduced to C3v or C2v respectively. It is important to note that figure 1 is given as a guide to represent the reduction in symmetry and we are not suggesting the molecule distorts in exactly this manner. Characters associated with each symmetry operation for each component of the icosahedral T1u LUMO can be found, and matched with the character table of the lower-symmetry point group to reveal any degeneracies. The result of this is that, with respect to a basis f x; y; zg defined such that the z component is perpendicular to the surface, the x and y form a doublet and the z is a singlet when the molecule is adsorbed with a pentagonal or hexagonal face prone to the surface. For all other adsorption orientations, three singlets are expected. It is therefore straightforward to model the effect this has on the molecule by constructing a simple diagonal Hamiltonian. To remain consistent with the JT

Hamiltonian in equation (1) the surface interaction is defined as:

$$\mathcal{H}_{sz} = -\frac{V_1^2}{\mu\omega^2}\begin{bmatrix} 0 & 0 & 0 \\ 0 & \Delta_2 & 0 \\ 0 & 0 & \Delta_1 \end{bmatrix}, \quad (3)$$

where the x component is treated as the zero in energy, and Δ2 and Δ1 are dimensionless parameters representing the energy difference between the x state and the y and z states

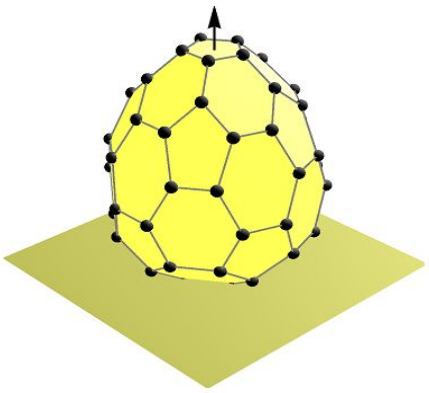


Figure 1. (Colour online) Representation of the reduction in symmetry introduced by a surface interaction on the pentagon prone molecule. Note that this is a visual aid to the symmetry reduction experienced by the molecule, and is not intended to be a real representation of the way the molecule distorts.

respectively. Thus, for orientations where a doublet remains, Δ2 will be equal to zero. By using this definition it is assumed that the strength of the surface interaction does not affect the basis functions at all, and merely changes the difference in energy between the different states. Comparing with DFT calculations undertaken by Pascual et al. [5] shows the H¨uckel method produces images that can't be distinguished from those from DFT. The surface interaction Hamiltonian in equation (3) acts in a basis where the z component of the LUMO relates to the perpendicular to the surface. In order to combine this Hamiltonian with the JT Hamiltonian which is written in terms of a 2-fold Z-axis, a simple transformation is needed to change to a common basis. Intermolecular interactions can be modelled via a splitting of the components of the LUMO in a similar manner to that described above for the surface interaction. When present as a monolayer, C60 molecules form a hexagonal lattice, and so, by working out what symmetry operations remain when a molecule is placed at each lattice point, the splitting of the orbitals can be found. It is assumed throughout that each molecule is oriented identically on the surface. While this is not always the case in practice, experimental data obtained on C60 monolayers indicates that this does occur in a lot of instances. It is therefore a good starting point for investigating the effects of intermolecular interactions. The orientation of molecules in a hexagonal lattice determines which of the symmetry operations associated with this group remain. The resultant point group symmetries for different molecular orientations are shown in table 1.
We note that aligning a reflectional plane of the molecule with a reflectional plane of the lattice results in a higher symmetry. Using this information it is again possible to construct a diagonal Hamiltonian to represent the induced splitting. However, for the instances where more than one T1u component is described by the same irrep., the resultant splitting in the electronic states can't be modelled using group theoretical ideas alone, as it is not known what linear combination of states represent the true singlets. As both the intermolecular and surface interaction Hamiltonians are diagonal and act on the same basis, it is sensible to combine them to form one Hamiltonian representing the external interaction. As the differences in energy between the molecular orbitals are not known and are varied as part of the investigation, the magnitudes of the splitting can be reduced to variables that represent the joint effect of the splitting induced by both the surface and intermolecular interactions.

Table 1. The reduction in symmetry of C60 molecules situated on a hexagonal lattice and the splitting of the T1u states f x; y; zg. Results are given for different molecular orientations. The column headed 'Reflection' indicates whether a reflection plane of the molecule is aligned with a reflection plane of a hexagonal lattice.

Orientation	Reflection	Symmetry	Splitting
Hexagon prone	Yes	D_{3d}	$\psi_x + \psi_y \rightarrow E_u$ $\psi_z \rightarrow A_{2u}$
	No	S_6	$\psi_x + \psi_y \rightarrow E_u$ $\psi_z \rightarrow A_u$
Double Bond prone	Yes	D_{2h}	$\psi_x \rightarrow B_{3u}$ $\psi_y \rightarrow B_{2u}$ $\psi_z \rightarrow B_{1u}$
	No	C_{2h}	$\psi_x \rightarrow B_u$ $\psi_y \rightarrow B_u$ $\psi_z \rightarrow A_u$
All other orientations	Yes	C_{2h}	$\psi_x \rightarrow B_u$ $\psi_y \rightarrow A_u$ $\psi_z \rightarrow B_u$
	No	C_i	All components transform as A_u

2.3. Results

The combined JT and external interaction Hamiltonians are a function of the two quadratic coupling constants V2 and V3, the vibrational coordinates Qγ, and the external interaction parameters Δ1 and Δ2. Diagonalising this Hamiltonian therefore provides a function in terms of these variables. Before looking at the effect on the STM current (and hence the STM image) the various parameters have, it is worthwhile considering the effect the external interaction has on the energy of the C□60 JT wells of different symmetry. For a single molecule (i.e. where no intermolecular interaction is present) only the surface interaction needs to be considered. For the hexagon and pentagon prone molecular orientations, x and y form a doublet, which means that Δ2 can be set to zero, so it is possible to look at the effects on the individual wells of Δ1 alone. The results of this are shown in table 2, where it can be seen that the JT wells form isoenergetic groups dependent on the orientation of the molecule. For the double-bond prone orientation, x and y are assumed to have negligible splitting in this table, although the calculation method also allows us to investigate the more general case where this is non-zero. The grouping of the wells has consequences when considering the resultant STM images as the distortion will tunnel between isoenergetic wells in finite JT coupling. Figure 2 represents the electronic states cx x+cy y+cz z for each JT well as points with coordinates fcx; cy; czg for (a), D5d, and (b), D3d type distortions, labelled with the molecular C2 Z-axis. The changes in the electronic states as the molecular distortion pseudorotates on a direct path between adjacent wells are shown as solid lines. As the pseudorotational process is expected to occur at a much faster timescale than that of an STM experiment, STM images will result from a superposition of all electronic states sampled. We will assume that the system spends most of its time in the wells and not consider the intermediate configurations, which will be a reasonable approximation for moderate coupling strengths (with appreciable barriers between wells). In fact, including intermediate configurations has been shown to have very little effect on the predicted images [10].

Table 2. Groupings of equivalent D5d, D3d and D2h JT wells for pentagon, hexagon and double-bond prone molecular orientations. Groups on the same row between braces are related to each other by reflections in the x–z plane. The groups that can be global minima in our model when Δ1 > 0 are marked with a + and when Δ1 < 0 with a _, assuming that Δ2 = 0 for the double-bond prone orientation.

	D_{5d}	D_{3d}	D_{2h}
Pentagon	C^+	$a,b,c\ g,i^+$	A,C,D,E,H
	A,B,D,E,F^*	d,e,f,h,j^*	B,F,K,L,O
			G,I,J,M,N
Hexagon	C,E,F^+	c^+	A,M,N
	A,B,D^*	$\{a,f,j\},\{b,e,h\}^*$	$\{B,D,J\},\{C,I,O\}$
		d,g,i	E,F,H
			G,L,K
Double-bond	C,D^+	a,b^+	A
	E,F^*	$\{e\},\{f\}^*$	F
	A,B	c,d	G
		$\{g,j\},\{h,i\}$	$\{E,I\},\{H,J\}$
			$\{B,N\},\{M,O\}$
			$\{C,K\},\{D,L\}$

To model the tunnelling current, a simple Tersoff-Hamann approach is used [9], which means that in our problem (for an s-type tip) the current will be proportional to the sum of the squares of the wavefunctions of each degenerate minimum-energy molecular orbital function i, i.e.:

$$I \propto \sum_i \psi_i^2. \qquad (4)$$

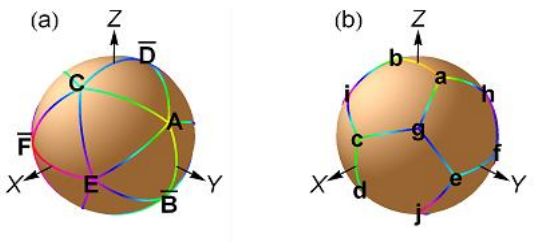


Figure 2. (Colour online) Representation of the electronic states cx x + cy y + cz z for each JT well as points with coordinates fcx; cy; czg. (a) is for JT parameters resulting in a D5d distortion, and (b) is for parameters giving a D3d distortion. The solid lines represent changes in the electronic states when the system pseudorotates on a direct path between nearest-neighbour wells.

Comparing the results in table 2, with the electronic states for the wells as shown in figure 2, it can be seen that for a positive value of Δ1 (i.e. a lowering of energy of the z state), it is the wells closest to the poles (with respect to a 2-fold Z-axis) which are favoured. For a negative value of Δ1, it is the wells closest to the equatorial X □ Y plane that are favoured. For the highly symmetric orientations considered in table 2, it is found that summing over

the squares of the lowest energy electronic states results in an STM image that is always constructed from some linear combination of the form ax 2 x + ay 2 y + az 2 z . This occurs because the wells are symmetrically distributed around the molecular Z axis, and hence when the current is found from the sum of the degenerate states, any cross terms will always cancel.

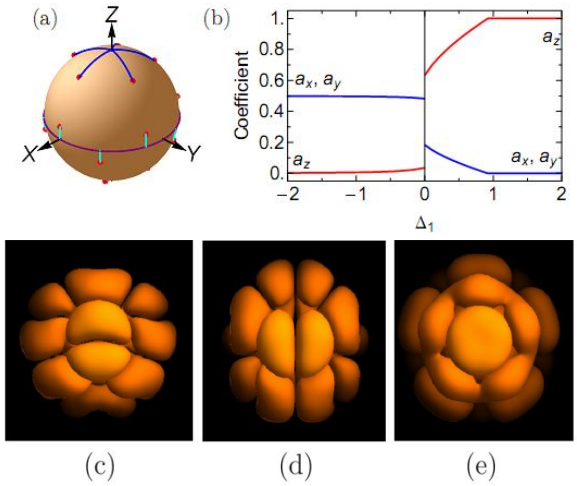


Figure 3. (Colour online) (a) Movement of the 'coordinates' fcx; cy; czg specifying the components of the electronic states as the strength of the external interaction Δ1 changes. The positions of the states evolve from those of the JT wells to either the poles or the equatorial plane, (b) variation of the coefficients fax; ay; azg in the expression for the tunnelling current I with the strength of the external interaction, theoretical STM scans of (c) 2 z , (d) 2 y and (e) 2 x. All results are for the pentagon prone molecule with JT parameters that favour a D3d distortion. An example of how the magnitude of the surface interaction affects the observed current is shown in figure 3, where the C60 molecule is oriented with a pentagonal face prone to the surface, and the JT coupling constants are chosen to favour a D3d distortion. Also shown are theoretical STM simulations of 2 x , 2 y and 2 z (calculated using HMO theory). The resultant STM image for any strength of surface interaction will result from a superposition of the appropriate contributions from each component. Although the exact form of such images must be determined by direct calculation, a rough indication of the expected results can be deduced from a visual examination of the results for the separate components. The crossover to a different solution when Δ1 = 0 indicates that a different group of wells become lowest in energy when the sign of the surface interaction changes. As indicated in table 2, wells fa; b; c; g; ig are favoured for a positive surface interaction, and wells fd; e; f; h; jg are favoured when the surface interaction is negative. This effect can be visualised by plotting the coefficients of the electronic state for each well, and seeing how the coefficients alter as the surface interaction changes, as is shown in fig. 3(a). It can be seen that choosing Δ1 > 0 such that the z component is lowered in energy relative to x and y causes the coordinates to shift towards the z axis of the sphere. Choosing Δ1 < 0 so that the energy of x and y are lowered causes the coordinates to shift towards the equator. It should be noted that the JT coupling constants are chosen to favour a certain symmetry for the isolated molecule, and do not represent the (lower) symmetry of the distorted molecule once the external interaction is considered. The introduction of the surface interaction generally reduces the symmetry to C2h.

2.4. Comparison with experiment

We will now consider published experimental results that may show a signature of the JT effect. The work presented in [11] shows images of a C60 monolayer on an alkylthiol buffer layer. While in [11], the molecules are assumed to be charge neutral, charge transfer between the molecule and substrate, or, as is particularly relevant when a buffer layer is present, between the molecule and tip, may result in images relating to the states of a charged ion, and as such the observation of images relating to the JT-distorted molecule should still be considered as a possibility. We start by seeking values for the coefficients fax; ay; azg that result in an image that matches the left-hand image in figure 1 of [11], reproduced here in figure 4(a). We find that the best match comes when we take the C60 molecule to be tilted in the y–z plane such that a molecular C2 axis is around 0.1 radians from the perpendicular to the surface and with fax; ay; azg _ f0; 0:13; 0:87g. The image resulting from this match is shown in figure 4(b). This is different to the match of the authors of [11], which is shown as an inset to figure 4(a). As our match is only a qualitative match by eye, determination of the coefficients is not exact; ay can vary between around 0.075 and 0.2 with corresponding changes in az between 0.925 and 0.8 [10].

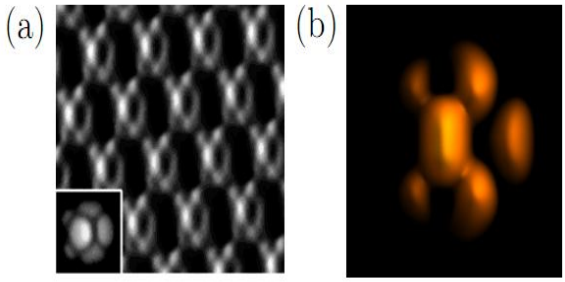


Figure 4. (Colour online) Comparison between (a) an experimental image obtained in ref. [11] (with theoretical interpretation from this reference inset), and (b) the theoretical STM image obtained using the method outlined here. (a) reprinted from figure 1 of LF Yuan et al. J. Am. Chem. Soc. 125, 169 (2003) [11]. Copyright 2003 American Chemical Society, Copyright (2003).

The next step in determining a theoretical match to the experimental image in [11] is to determine whether it is possible to find combinations of the JT and external interaction parameters that result in the

required form for the current I. It is found that this is indeed possible for a range of JT parameters that favour D3d wells a and b, alongside external interaction parameters that set the z state of a double bond prone molecule lowest in energy. Also, it is important to note that we can't get our match without using a JT model, as it is only when we superimpose results due to different distortions that unwanted cross-terms in the expression for I cancel. Hence our match represents a different physical situation, and isn't simply an alternative explanation of the same case. It is worth noting that the tilt in the y–z plane needed to match the experimental image reduces the symmetry associated with both the surface interaction and the intermolecular interaction (as one of the reflection axes of the molecule is lost, which previously aligned with one of the lattice). This introduces the problem where two of the components are described by the same irrep., and as such the correct combination of states needed to describe the splitting can't be determined from group theory alone. However, as the deviation from the double bond prone case is small, the assumption is made that the components split in the same way as for the double bond prone molecule. The fact that an accurate match with experiment is found shows that this assumption appears valid.

3. Higher charged states

So far, only the C□60 monoanion has been considered. However, experimental images are available for C3□ 60 , C4□ 60 [12], and C5□ 60 [13] ions as well. Investigating the higher charge states is inherently more difficult due to the Coulomb interaction between the electrons, which affects the electron distribution around the molecule and hence the observed current during STM. Due to electronhole equivalence, the JT effect in C5□ 60 is the same as in the monoanion. As such this doesn't need further consideration. This work will concentrate on the C4□ 60 anion, which is modelled as two interacting holes, and is considered by looking at the T1u T1u interaction, which results in Ag _ Hg antisymmetric states and a T1g symmetric state [2]. The coupling between the T1g state and the Hg vibrational state is the same as for the monoanion and so only the coupling with the antisymmetric state will be considered here. The C3□ 60 ion may also be modelled by considering the product T1u T1u T1u, resulting in a JT effect between the hg vibration, and the T1u _ Hu electronic states [14]. However, this will not be considered here. It is found that for the hexagon and pentagon molecule, a component of the Hg state transforming as the spherical harmonic d3Z2□R2 is a singlet, with components transforming as dX2□Y 2 and dXY forming one doublet and the components transforming as dY Z and dZX forming a second doublet. For all other orientations, five singlets transforming as the above d-orbitals are formed. Note that this basis is defined differently to the JT basis, which uses linear combinations Hgθ and Hgϵ of d3Z2□R2 and dX2□Y 2 as defined in equation (2) and in [15]. Therefore an additional transformation needs to be made to align the external interaction and JT Hamiltonian bases. The states transforming as dyz, dzx and dxy will be called Hg4, Hg5 and Hg6 respectively. Clearly additional parameters are introduced due to the combined Coulomb and external interactions compared to C□60 due to the larger dimension of the electronic basis, as each distinct state needs to be set at a different energy. Also, where there are repeated representations in the symmetry reduction, we do not know from group theory alone what basis states to take for the external interaction Hamiltonian. However, a unique form can be written down from knowledge that the single-hole states x, y and z will be at different energies to each other. We note that [16] gives values for the term splitting between the A and H states due to the Coulomb interaction. Using an estimate for the linear coupling constant in [17] to convert the values to the units used here leads to a value for the term splitting of 2:4. We will use this value to illustrate our results below. However, appropriate values for the real C60 system could vary somewhat from this. In order to obtain expressions for the current that would be observed during STM, we express the two hole basis states in terms of the single hole molecular orbital functions. The hole interaction transforms as T1u T1u, thus, by using the Clebsch-Gordon coefficients in [15], the correct combinations of the two hole states can be constructed. This can then be combined with the correct spin state to produce the appropriate two-hole states. To obtain an expression for the observed STM current, the square of some combination(s) of the basis states needs to be taken. This introduces problems due to the inclusion of the electron spin in the wavefunctions. To solve this, it is noted that the distribution of one electron around the molecule is dependent on the position of the second electron. It is therefore possible to integrate over all space for one of the electrons to obtain the current in terms of a single electron distribution function. The orthonormality of the states ensures that the integrals that arise from the products of the various states always go to one or zero, resulting in a simple expression that is made up of the single electron molecular orbitals only. With a form obtainable for the effective current, it is then possible to investigate the effect of the surface and Coulomb interactions on observed STM images. In much the same way as was obtained for the monoanion, groupings of JT wells occur, and, despite the fact that the basis is now formed from a two hole combination, the images are again constructed from some linear combination of the squares of the single hole (electron) molecular orbitals for the high symmetry orientations. However, a particular well will provide a different contribution to the current when compared with the monoanion,

and as such the resultant images are different. Figure 5 shows an example where the molecule is situated with a pentagon prone to the surface, with JT coupling constants chosen to prefer a D3d molecular distortion. In the figure, the energy of the A state has been set to 2:4 relative to that of the Hgθ state, the splitting between Hgθ and the Hg4;Hg5 doublet, denoted Δ2, is taken to be 0, and the splitting between Hgθ and the Hgϵ;Hg6 doublet, denoted Δ1, is varied. It can be seen that in the asymptotic limit of a strong surface interaction, the current is still formed from all of the molecular orbital functions, with none tending to zero. This is because the two hole states Hg4, Hg5 and Hg6 are formed from states where the two holes are never in the same single-hole orbital. As such, any state involving these two-hole states will always contain contributions from 2 x , 2 y and 2 z . This means that observed STM images are in general likely to be less distinctive than those from the monoanion. However, the current is still made up from contributions from 2 x, 2 y and 2 z with no cross-terms.

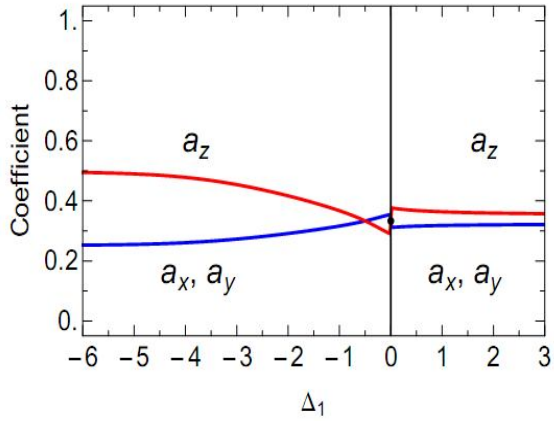


Figure 5. (Colour online) Graphical representation of the coefficients of the square of the single electron molecular orbitals, with varying strength of surface interaction parameter Δ1 for the pentagon prone molecule with JT parameters to favour a D3d distortion. Using this idea, it is possible to obtain a match with the experimental image obtained by Wachowiak et al. [12]. The best match, shown in figure 6, arises from a molecule in the doublebond prone orientation and with a current I _ 0:015 2 x + 0:985 2y.

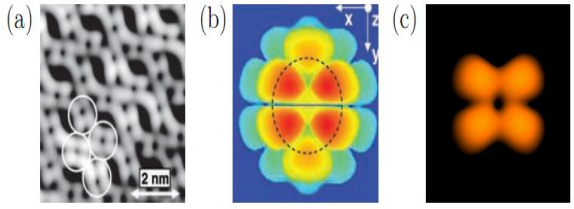


Figure 6. (Colour online) Comparison between an experimentally obtained image and the theoretical interpretation in [12] (a and b), and the best-fit image obtained by matching the current to I _ 0:015 2 x + 0:985 2 y (c). (a) and (b) are reprinted from parts of figures 3 and 4 of [12] with permission from AAAS.

The next step in the identification of the origins of the image is to determine what values of the JT and surface interaction parameters could produce the required current. Examination of our graphs of the contributions from 2 x , 2 y and 2 z shows that the only situation that can result in the required current is if the JT parameters prefer a D3d distortion, with the external interaction picking out wells e and f. The magnitudes of the coefficients of x and y are the same for these two wells, but the signs are different. We can therefore conclude that the required combination of 2 x and 2 y occurs if wells e and f are taken to have electronic states 0:122 x _ 0:992 y respectively. It is found that a wide variety of the external interaction parameters and quadratic coupling constants result in this state. It is noted that in order to obtain a match which contains only the x and y single electron states, the states can't involve Hg4, Hg5 or Hg6 (for the reasons mentioned above), which means that these states must be higher in energy than the Hgθ and Hgϵ states. As the external interaction for the double bond prone molecule splits the Hg state into 5 singlets, the assumption can be made that the external interaction is such that these are suitably higher in energy and so don't contribute to the problem. Our match to the image in [12] is obtained from JT parameters preferring a D3d distortion, but once the surface and Coulomb interactions are included, the result is a dynamic distortion of C2h symmetry. This is different to the interpretation in [12], where the image was explained by a static JT distortion of D2h symmetry. This corresponds to a sole contribution from the y component in our notation, and corresponds to an image with a nodal plane (seen as in the horizontal division of the image in figure (6)(b) into two halves and the similar vertical division in figure 3(d)) which is not present in the experimental image. However, the evidence that our match is more appropriate than that given in [12] is not conclusive as factors such as experimental blurring could produce a similar effect to the inclusion of a small x component in the states. We note that previous work on the p2h JT system that describes this anion suggests that isolated C60 molecules should not favour D2h distortions, and instead distort to either D3d or D5d [2]. Studies of isolated ions in a storage ring indicate that the distortion is most likely to be to D3d symmetry [18], as did an analysis of spectra from electrochemically-generated C60 ions in solution [17]. However, the evidence is again not conclusive.

CONCLUSION

In this work, a method has been introduced to model the STM images produced for the JT active ions of C60 when present on a surface, either individually, or as part of a monolayer. This method utilises group theoretical techniques to model the reduction in symmetry of the molecule due to both interactions

with the surface and from interactions with nearest neighbours (when present). It is found that for C□60, C2□ 60 and C4□ 60 ions, the resultant STM current I is always formed from a linear combination of 2 x, 2 y and 2 z when the molecule is situated with a C2;C3, or C5 symmetry axis prone to the surface. Matches with experimental images have been obtained for both C□60 and C4□ 60 anions. In both cases, our interpretations are different to those in the original works. Clearly, the work given here is a starting point for future investigations. Only a small selection of orientations and JT parameters have been looked at, and particularly in the case of C4□ 60, the effect of a number of different external interaction parameters still need to be explored. However, the method can easily be extended to look at these cases. In addition, the C3□ 60 case, which has not been looked at here, also needs to be investigated, although incorporating the external interactions in this case is more complicated due to the presence of repeated irreps. Experimental data also exists for this anion [12]. A hindrance in expanding on this work is the lack of experimental images within the literature. It is hoped that as experimental techniques continue to improve, additional data will soon become available to firstly verify the findings here, and secondly to examine the effect of different orientations on the images. In doing so, it is hoped that clear indications of the JT effect will be observable through interpretation of the experimental images.

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