# CHARGE-TRANSFER SHAKE-UP SATELLITES ACCOMPANYING CORE IONIZATION IN ORGANIC DONOR/ACCEPTOR MOLECULES: BIS(4-DIMETHYLAMINOPHENYL)SQUARAINE AND ITS DERIVATIVES

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## ABSTRACT

Solid state XPS spectra of bis(4-dimethylaminophenyl)squaraine and a number of derivatives are presented. The complex multipeak N1s and O1s satellite spectra are analyzed in terms of intraand inter-molecular contributions and related to corresponding electronic transitions of the neutral species. It is concluded that a distinctive low-energy O1s satellite characterizes the intermolecular excited state charge transfer between the donor and acceptor fragments on adjacent overlapping sites. A CNDO/S(S + DES CI) equivalent-core computation on O1s ionization of the parent monomer supports this interpretation. Spectral comparisons indicate that chemical substitution to yield intramolecular hydrogen bonding may provide a more favorable pathway for O1s core-hole screening, and thus inhibit intermolecular charge-transfer. The broad asymmetric C1s signals are shown to reflect a wide spread of chemically shifted carbon sites characteristic of a highly charged polarized monomer unit. The consequences of adsorbed  $O_2/H_2O$ on the spectral properties and electronic conductivity are discussed.

#### INTRODUCTION

Bis(4-dimethylaminophenyl)squaraine and related organic molecules are of considerable interest for their applications in electronic devices [1-7]. This is due particularly to their intense long wavelength absorption in the solid state. Crystallographic studies have shown that this class of highly polar donor/ acceptor systems form overlapping structures with typical interlayer spacing as short as ~3.35 Å [5, 8]. Such solid state bonding is favorable for intermolecular  $\pi$ -orbital overlap [5, 8]. Optical measurements indeed indicate a weak intermolecular charge-transfer excitation near the intense long wavelength monomer-like transition (~1.78 eV [8]). Similar parallels between solid state pairing and optical properties have recently been reported for other highly polar organic systems [9, 10].

In this work the complex multipeak O1s, N1s and C1s hole-state spectra of

bis(4-dimethylaminophenyl)squaraine, SQ(H), and a number of derivatives are presented and discussed in terms of intra- and intermolecular contributions.



The "quinoid" structure has been verified experimentally for bis(methoxyphenyl)squaraine [11, 12] and is reflected by quantum chemical geometry optimization for SQ(H) [13] and bis(methoxyphenyl)squaraine [14].

Previous experimental and computational studies on the vapor and condensed phases of complex organic systems indicate that XPS can be a useful probe of intermolecular interactions [15, 16]. Under suitable structural constraints, the response of a highly polarizable  $\pi$ -electron framework to the localized core-hole created in an adjacent molecule can lead to satellite features, or shake-up (SU) states, whose energies and intensities reflect specific channels for intermolecular coupling [15, 16]. The crystalline pairing of the squaraines satisfy the conditions for which core-hole-enhanced intermolecular charge-transfer is favorable [17]: (1) the bonding is "weak" in the neutral solid such that the valence electron wavefunctions maintain local site (monomerlike) character [8]; and, (2) the donor nitrogen of one molecule lies almost over the center of the strongly electron-accepting  $C_4O_2$  squaraine ring of an adjacent site [5, 8]. Mixing of the adjacent monomer orbitals by the core-hole perturbation on one unit to form localized dimer-like wavefunctions has been identified as being the origin of spectral differences between the gas and condensed phase of model donor/acceptor molecules [15, 16, 18].

## EXPERIMENTAL

The materials studied were synthesized from squaric acid (A-route) as described previously [19]. Spectra obtained from SQ(H), synthesized from di-nbutyl-squarate (E-route), are included for comparison [19]. Elemental analyses (C, N, F, H) were consistent with the ideal structures to within  $\sim 0.2\%$ .

XPS measurements were performed on pressed pellets using a modified AEI ES200B photoelectron spectrometer fitted with a Al  $K\alpha_{1,2}$  source  $(\lambda v = 1486.7 \text{ eV})$  operated at 10 kV and 60 mA. Typical analyzer and source chamber operating pressures were  $\sim 7.0 \times 10^{-7}$  and  $\sim 2.0-4.0 \times 10^{-8}$  torr, respectively. The energy analyzer was operated using a fixed retarding ratio (FRR mode). Elemental ratios,  $N_i/N_j$ , were semiquantitatively determined from the relationship

$$\frac{N_{\iota}}{N_{j}} = \left(\frac{\sigma_{j}}{\sigma_{\iota}}\right) \left(\frac{\mathrm{KE}_{j}}{\mathrm{KE}_{\iota}}\right)^{3/2} \left(\frac{I_{\iota}}{I_{j}}\right)$$
(1)

where  $I_{i(j)}$  are the integrated areas of the respective signal displays and  $\sigma_{i(j)}$  are the photoemission cross sections. The kinetic energy factor (KE) is obtained by combining the kinetic energy dependence of the elastic mean free path of the escaping photoelectrons ( $\lambda \propto \text{KE}^{1/2}$  [20, 21]) and the energy analyzer transmission coefficients for the FRR mode ( $f_i \propto \text{KE}^{1.0}$  [22]). Scofield theoretical cross sections were used for data reduction [23]. Each level was scanned over an energy range of 20.0 eV, sufficient to establish base lines for intensity comparison.

Data are presented as-received from the spectrometer without smoothing or background subtraction. Spectral outlines were hand-drawn through the best estimates of the average signal. Peak areas were obtained by averaging several planimeter traces of the profile taken on enlarged spectra. In certain cases well-developed multipeak structure, peak asymmetries and/or peak widths suggested specific deconvolution. Such data reductions were accomplished based on reasonable assumptions of component binding energies and peak widths.

## COMPUTATIONAL

Computations were performed within the semiempirical all-valence-electron closed-shell CNDO/S formalism [24, 25], including up to doubly-excited configurations [26]. The Pariser-Parr approximation to the two-center coulomb repulsion integrals was used [27, 28]. Core-ionization was treated within the equivalent-core approximation [29, 30], where the atom to be ionized (atomic number Z) was replaced by the next highest atom in the periodic table (Z' = Z + 1). In the ionic state calculations, configuration interaction was performed on the 300 lowest-energy excitations to obtain shake-up energies. These included energy-selected single and double excitations, obtained from 5000 created configurations, which were spin-adapted within the singlet manifold of the closed-shell of valence electrons [26]. Although this approach involves making a number of approximations, the results have been shown to adequately simulate the response of the valence electrons toward the core-hole in a variety of organic donor/acceptor molecules [15, 16, 18, 31-34].

Shake-up intensities were calculated by projection of the correlated (CI) ion state wavefunctions onto the "uncorrelated" single determinant wavefunction of the neutral system according to the sudden approximation [35–37]

$$I_i \propto |\langle \Psi_{\rm F}(i)|\Psi_{\rm GS}^{\rm HF}(N)\rangle|^2 \tag{2}$$

where

$$|\Psi_{\rm F}(i)\rangle = \sum_{j} C_{ij} \Phi^{a,d}_{b,c}(i,j)$$

 $C_{ij}$  are the excited state CI coefficients obtained in the energy calculation.  $\Phi_{b,c}^{a,d}(i, j)$  are the spin-adapted configurations constructed from single determinants,  $D_{b,c}^{a,d}(i, j)$  or (a,b||c,d), where  $a \to d$  and  $b \to c$  orbital excitation has



Fig. 1. C1s, N1s and O1s spectra of SQ(H)-A, SQ(H)-E and SQ(CH<sub>3</sub>)-A. Assignments of the components in the N1s and O1s spectra are indicated in the top panel. The hatched component in the O1s spectra emphasizes the term associated with "excess" oxygen, as described in the text. The dashed lines in the C1s spectra are used to symmetrize the intense main peak and are used only to locate the "center" for binding energy referencing.

**BINDING ENERGY (eV)** 

400 0

410 0

540 0

530 0

occurred relative to the closed-shell ion ground state (0,0||0,0). In the present application  $\Phi_{b,c}^{a,d}(i,j) \sim D_{b,c}^{a,d}(i,j)$  and the ionization intensities are evaluated as summations over the determinantal overlaps,

$$I_{\iota} ~ \propto ~ \sum\limits_{j} ~ C_{\iota j}^2 |\langle D_{0,0}^{0,0}(N) | D_{b,c}^{a,d}(i,j) 
angle|^2$$

285 0

Molecular coordinates for SQ(H) were taken from a previous MNDO geometry optimization [13].

295.0



Fig. 2. C1s, N1s and O1s spectra of two different preparations of SQ(F)-A. The O1s contribution attributed to "excess" oxygen is shaded (see text). Cursory scans of the F1s region (A1 and A2) gave single peaks at BE = 686.8 eV.

## EXPERIMENTAL RESULTS

Figures 1-3 show the experimental spectra of the seven squaraines considered. The spectral profiles were stable to long term analysis, i.e. X-ray exposure and high vacuum pumping. Radiation damage or structural degradation can therefore be excluded as the origin of the multipeak structures and signal broadening. Binding energies are referenced to the center of the broad C1s peak, taken as 285.0 eV. This referencing gives a binding energy for the main N1s peaks of ~ 399.5 eV. This is in accord with the N1s binding energies found for related aminophenyl-substituted squaraines using independent calibration methods [38], and for phenyl-substituted amines [39, 40]. The very broad C1s signals ( $\Delta BE ~ 3.0-3.3 \text{ eV}$ ) are consistent with the findings of Neuse and Green on related squaraines [38], and with XPS studies on other highly substituted aromatics [34, 41].

Semiquantitative elemental ratios from eqn. (1) give  $N_{\rm C}/N_{\rm N}$  within  $\pm 10.0\%$  of the stoichiometric values. The moderately intense N1s satellites shown in Figs. 1-3 are attributed to multielectron or shake-up processes. These appear uniformly at ~ 2.1 and 3.6 eV above the main peak for SQ(H)-A and E, and SQ(CH<sub>3</sub>). There is some variation in the satellite/mean peak separations for



Fig. 3. C1s, N1s and O1s spectra of SQ(OH)-A, and the C1s and O1s spectra of SQ(OCH<sub>3</sub>)-A. The SQ(OCH<sub>3</sub>) N1s region was inadvertently neglected in the data runs. The O1s contribution attributed to "excess" oxygen is shaded. The single-component O1s terms assigned to hydroxy and methoxy ionizations are identified (see text).

SQ(F), although the number of satellites and their relative intensities parallel those of Fig. 1. A third, higher-energy, SU peak appears in the N1s spectrum of SQ(OH) (Fig. 3). The main peaks contain 60.0–65.0% of the N1s intensity integrated over the displayed energy range. The first satellite/main peak intensity ratios are nearly constant at ~0.34.

The  $N_{\rm C}/N_{\rm O}$  ratios evaluated from eqn. (1) vary over a wide range. On an absolute scale the O1s intensities are too large to reflect the elemental ratios by factors of 1.2 (SQ(OH)) to 1.6 (SQ(CH<sub>3</sub>)). In the first attempt to resolve the O1s spectral profiles it was assumed that the deviation of  $N_{\rm C}/N_{\rm O}$  from the stoichiometric values reflected an adsorbed ("excess") oxygen species. It was further assumed that this "excess" oxygen would give rise to a single peak which would occur at nearly constant binding energy throughout the series. Initial deconvolution was performed on the O1s spectra of the two SQ(H) preparations (Fig. 1). SQ(H)-A has the most "excess" oxygen and shows a distinct higher binding energy maximum (BE ~532.2 eV). This is reduced to only a shoulder on going to SQ(H)-E which has correspondingly less "excess" oxygen. In neither case are the first peaks in the experimental spectra, labeled

Main in Fig. 1, sufficiently intense to account for all of the "stoichiometric" oxygen.

Components were drawn to represent the Main peaks and the two weaker terms in the high energy tails and were held at fixed binding energy. The "excess" oxygen contributions (from eqn. (1)) and the single peaks drawn to account for the remainder of the "stoichiometric" oxygen were then varied in binding energy to obtain a consistent fit to the experimental profiles. This resulted in identical distributions of the "stoichiometric" oxygen between the main and satellite features.

Assignments of the five peaks thus used to resolve the SQ(H) O1s spectra are given in Fig. 1. The three SU terms account for ~38.0% of the stoichiometric intensities. This is in near accord with the main/SU intensity distribution found for N1s ionization. Again, the first satellite/main peak intensity ratios are nearly constant at ~0.37 (~0.34 for N1s). The energy of the first SU peak, however, is ~1.0 eV closer to the main peak for O1s ionization: ~1.2 eV, vs. ~2.1 eV for N1s ionization. This procedure was similarly employed for the O1s profiles of SQ(CH<sub>3</sub>) and SQ(F) where identical main/SU ratios were used to distribute the "stoichiometric" intensities (see Figs. 1 and 2).

This procedure was extended to the hydroxy and methoxy analogs. The "stoichiometric" squaraine and substituent oxygens were assumed to contribute equal intensities, and the "excess" assigned to a single peak at 533.0 eV, as before. The substituent oxygen intensities were likewise assigned to a single peak. The O1s profile of the methoxy analog was deconvoluted by adding to the "excess" component the same main peak/SU structure for the squaraine oxygen as used in Figs. 1 and 2 — relative intensities and absolute binding energies. The binding energy of the single substituent term was then adjusted to best fit the spectrum, resulting in a value for BE (OCH<sub>3</sub>) of  $532.0 \,\mathrm{eV}$ . Binding energies for the single component "excess" and substituent oxygens used to resolve the hydroxy spectrum were taken from the methoxy fit as 533.0 and 532.0 eV, respectively. Due to the apparent shift of the leading edge of the SQ(OH) O1s profile to higher binding energy, the remaining area could not be accounted for with the main peak/SU intensity and energy distribution for the squaraine oxygens used before. The best fit within the above constraints is shown in Fig. 3. The main peak contains  $\sim 80.0-85.0\%$  of the squaraine O1s intensity, compared to  $\sim 60.0\%$  for the other molecules considered.

Attempts to fit the SQ(OH) O1s spectrum beginning with the previous main peak/SU distribution for the squaraine oxygen yielded a more gradual low binding energy slope, characteristic of the methoxy analog. This required a shift in the O1s<sub>OH</sub> peak to lower binding energy to build the leading edge intensity back up. A distinct shift in the maximum of the theoretical profile to lower binding energy results, concomitant with the appearance of a shoulder on the trailing edge. Deconvolution using other variations in the peak distribution was not attempted.

Variations in the O1s spectral profiles of the seven squaraines of Figs. 1-3 are thus semiquantitatively reflected by variations in the intensity of a single

peak near BE = 533.0 eV containing the amount of "excess" oxygen calculated from eqn. (1).

The first moment,  $M_i$ , of the intensity distribution arising from a given core-ionization (main plus satellite features) is equal to the Koopmans' ionization potential, or the binding energy of the core level in the neutral molecule [35, 37, 42]

$$M_{i} = \sum_{i} \left( I_{i} \times E_{i} \right) / \sum_{i} I_{i}$$
(3)

The deconvoluted squaraine fragment O1s spectra of Fig. 3 yield  $M[SQ(OCH_3)] = 531.04 \text{ eV}$  and M[SQ(OH)] = 531.71 eV, assuming  $\Sigma I_i$  is the same in both cases. The apparent shift of the main (first) peak to higher binding energy (~0.3 eV) on going from SQ(OCH<sub>3</sub>) to SQ(OH) is not caused simply by the redistribution of main peak/SU intensity: it is present already at the neutral molecule level.

This shift in the leading edge of the SQ(OH) O1s spectrum to higher binding energy is consistent with expected intramolecular hydrogen bonding interactions between the hydroxyl group and the squaraine oxygen. Substituents which place positive charge centers near the squaraine oxygen appear to reduce intermolecular bonding forces and/or increase intramolecular stability. The hydroxyl and methyl derivatives, for example, can be vacuum sublimed to yield thin films, whereas other analogs decompose in the vapor phase [1]. The strong SU peak at  $\sim 1.2 \,\mathrm{eV}$  in the parent fragment O1s spectra of SQ(H).  $SQ(CH_3)$ , SQ(F) and  $SQ(OCH_3)$  is thus taken as a distinctly solid state manifestation. The apparent absence of this term in the SQ(OH) spectrum suggests that the O1s core-hole can more easily draw screening charge intramolecularly through the hydrogen bonding bridge than from an adjacent molecule. The possibility that intramolecular hydrogen bonding in SQ(OH) competes with strong intermolecular or external solvation interactions has been noted in studies of squaraine morphological properties [43]. As shown below, our interpretation, that the squaraine fragment O1s distribution of SQ(OH) reflects monomer-like character, is supported by the results of quantum chemical computations.

The O1s binding energies of the squaraine compounds parallel those of other strongly polar molecules. The O1s binding energy of condensed p-benzoquinone (PBQ) is 530.8 eV [44], whereas that of hydroquinone is 532.2 eV [44]. These values are within 0.3 eV of the binding energy of the oxygen of the squaraine fragments (main peak), and the hydroxy and the methoxy substituents, respectively. The low O1s binding energy of the hydroxy and methoxy groups reflects attachment to a highly polarizable framework. By comparison, the O1s binding energy of p-methoxy-substituted polystyrene is 534.2 eV [45]. A comparison O1s binding energy for the hydroxy group in phenol of ~533.7 eV can be inferred from the gas phase  $\Delta BE$  (O1s-C1s) results of Ohta et al. [46]. The SQ(F) F1s binding energy (caption, Fig. 2) is likewise significantly shifted below that observed in condensed fluorobenzene by ~2.8 eV [47]. It has been shown through correlations with charge-potential calculations that the F1s binding energy is significantly more sensitive to charge density variations than are C1s and O1s [47]. The very low binding energies of the O1s and F1s peaks support the proposed zwitterionic character of the squaraine structure [1].

The "excess" oxygen in Figs. 1–3 is tentatively attributed to adsorbed  $O_2$  and/or  $H_2O$  as found in studies of various other polar organic molecules. Water, in fact, is a reaction by-product of both the acid (A) and the ester (E) synthetic routes to squaraine preparation [43]. If adsorbed  $H_2O$  is the origin of the squaraine "excess" oxygen, the O1s binding energy (~533.0 eV) appears ~ 1.6–2.0 eV below that previously reported for this species. Dilks, for example, found a BE(O1s) value of 534.4 eV for  $H_2O$  adsorbed or trapped in polymers [48].



Fig. 4. Comparison of the experimental N1s and O1s (squaraine fragment) spectra of SQ(OH) from Fig. 3 with the CNDO/S (CI) equivalent-core computations on the SQ(H) monomer. See Tables 1 and 2 for our interpretation of the theoretical spectra. The hatched line connecting the O1s spectra is drawn at the energy of the calculated lowest-lying  $\pi^* \leftarrow \pi$  shake-up state. As discussed in the text, this transition from the highest occupied (HOMO) to the lowest unoccupied (LUMO) orbital does not interact with the ground state due to symmetry differences. Thus, this state contributes zero intensity in the core-hole spectrum.

Wilson and Collins observed "excess" oxygen at 537.0 (main peak) and 535.0 eV (shoulder) in phthalocyanine thin films [49]. Re-examination of previous data on substituted pyrylium cations which exhibited "excess" oxygen gave a BE(O1s) value of 534.5 eV, relative to the center of the C1s band taken as 285.0 eV [34].

Adsorbed  $O_2/H_2O$  has been shown to enhance the surface conductivity of phthalocyanines [49, 50]. Relative to the two oxygens of the squaraine moiety, SQ(H)-E has the least amount of adsorbed oxygen of the seven molecules considered. 4-probe conductivity measurements (ambient air) on pressed pellets gave  $\sigma(E) = 2.22 \times 10^{-9} \Omega^{-1} \text{ cm}^{-1}$ SQ(H)-E and SQ(H)-A and of  $\sigma(A) = 2.90 \times 10^{-8} \Omega^{-1} \text{ cm}^{-1}$ . By way of comparison, Loutfy and co-workers measured the dark conductivity of a particle dispersion of SQ(H)-A in a polymer binder using a photovoltaic cell and found  $\sigma(A) = 1.5 \times 10^{-8} \Omega^{-1} \text{ cm}^{-1}$ [6]. The enhancement of conductivity on going from E to A is consistent with an increase in the relative  $O_2/H_2O$  content. The XPS spectra of SQ(H)-A are consistently broader than those of SQ(H)-E, possibly as a consequence of the greater oxygen/water content. Improvements in the xerographic properties of SQ(H),  $SQ(CH_3)$ , SQ(F) and SQ(OH) were found on going from the acid to the ester synthesis [43]. Figure 2 shows, however, that the amount of adsorbed oxygen can vary considerably even between preparations following the same synthetic route. The relative amounts of adsorbed  $O_2/H_2O$  found by XPS and its presumed effect on the electrical properties is consistent with arguments based on morphological differences [43].

## COMPUTATIONAL RESULTS

The CNDO/S (CI) hole-state calculations on SQ(H) are compared with the experimental N1s and O1s spectra, considered to best approximate the spectra expected of the monomer, in Fig. 4. In both cases, the computational profiles reflect the experimental structure, although the intensities of the low-lying SU states are somewhat underestimated. This appears most critical for the first N1s shake-up state which is calculated to be ~ 0.6 eV higher in binding energy than is actually observed (see discussion below). This SU feature is essentially the one-electron  $\pi^* \leftarrow \pi$  HOMO  $\rightarrow$  LUMO excited state and occurs with more than 3 times the ionization intensity of any higher-lying term, as may be seen in Table 1. Moderately intense SU has been reported for N1s ionization of the dimethylamino donor group substituted into highly polar organic molecules, and is attributed to intramolecular interactions [34]. Due to the prohibitive size of the squaraine framework, we were unable to use dimer models to probe possible solid-state SU intensity enhancements as has been done previously [15, 16, 42, 51].

Ionization of acceptor group heteroatoms commonly yields the strongest  $\pi^* \leftarrow \pi$  HOMO  $\rightarrow$  LUMO SU transitions found in organic D<sup>+</sup>-Ar-A<sup>-</sup> donor/ acceptor molecules — the nitro group N1s and O1s ionization of p-nitroaniline

#### TABLE 1

Results of computations on the SQ(H) N1s monomer core-hole spectrum. The final-states of interest with normalized ionization intensities are given. Also tabulated are the CI contributions of the Hartree-Fock equivalent-core ground state and the primary ion-state determinants and their overlap with the neutral molecule SCF determinant,  $|\Psi_{GS}(N)\rangle$ .  $E_{conf}$  are the configuration energies after spin-adapting the determinant within the singlet manifold of the closed-shell valence structure. The relevant orbitals are given in Fig. 5 The determinant representation in the wavefunctions corresponds to the spin-adapted configuration.

Final-st	ate distribution (N1s)		Wavefunction (CI vector)	
State	(0,0∥0,0)CI coeff.	$\left \left<\Psi_{\mathrm{F}}(I)\right \Psi_{\mathrm{GS}}(N) ight> ight ^{2}$ (%)	$E_{\rm F}$ (eV)	
1	0.9689	100 0	0.00	0.9689 (0,0  0,0) - 0.1284 (61,61  62,62) +
2	0.0014	0	2 60	0.9144 (0.58    62,0) - 0.1545 (0.58    63,0) +
3	0 0005	6.6	2 93	0.9439(0.61    62.0) + 0.1060(0.60    62.0) +
4	-01135	0.9	3 69	-0.1135(0,0  0,0) + 0.7783(0.60  62,0) +
5	0 0705	1.9	4 26	$0\ 2820\ (0,60\ 62,0)\ +\ 0\ 7494\ (0,61\ 63,0)\ +\ \ldots$
7	0 0468	0.7	5 12	
10	0 0260	0.9	5 77	
11	- 0.0379	1.8	5.77	$\sim 0.2022$ (0,60  62,0) $ -  0.3265$ (61,61  62,62) +
Contrib	iting determinants			
Order	Determinant	$\langle D^{a,d}_{b,c}(\jmath) \Psi_{\rm GS}(N)\rangle$	$E_{\rm conf}$ (eV)	
1	(0,0  0,0)	0 8053	0.00	
2	(0,61  62,0)	0.1948	3.11	
3	(0,58 62,0)	0.0007	3 18	
4	(0,60  62,0)	0.0745	4.52	
7	(61,61 62,62)	0.0471	5.88	

(PNA), for example [52–55]. As is shown in Table 2 and emphasized in Fig. 4, O1s ionization of the SQ(H) monomer does not follow this trend. Although the  $\pi^* \leftarrow \pi$  HOMO  $\rightarrow$  LUMO transition yields the intense low energy neutral molecule absorption, this state does not couple with the O1s core-hole ground

## TABLE 2

Results of computations on the SQ(H) O1s monomer core-hole spectrum (see caption to Table 1)

Final-sta	ate distribution (O1s)		Wavefunction (CI vector)	
State	(0,0∥0,0)CI coeff.	$ \langle \Psi_{\mathbf{F}}(I) \Psi_{\mathbf{GS}}(N)\rangle ^{2}$ (%)	E <sub>F</sub> (eV)	
1	- 0.9896	100.0	0.00	- 0.9896 (0,0  0,0) + .
2	0	0	2.29	$0.9359 (0,61 \  62,0) + 0 1073 (0,60 \  63,0) + \ldots$
4	0.0979	2.6	3.38	$0.8571(0,60  62,0) - 0.1231(0,61  63,0) + \dots$
8	-0.0275	4.0	4.18	$0.2109(0,60\ 62,0) + 0.8095(0,61\ 63,0) + .$
43	0.0056	31	7.19	$\sim 0.6076 \ (0,57\ 63,0) \ - \ 0.2046 \ (0,61\ 68,0) \ +$
Contribu	uting determinants			
Order	Determinant	$\langle D^{a,d}_{b,c}(j) \Psi^{ m HF}_{ m GS}(N) angle$	E <sub>conf</sub> (eV)	
1	(0,0  0,0)	0.7829	0.00	
2	(0,61  62,0)	0	3.11	
6	(0,60  62,0)	0 0952	4.49	
7	(0,61  63,0)	0 1569	4.68	
26	(0,57  63,0)	0 1362	7.19	
48	(0,52  63,0)	0.1249	8 17	

state to give satellite intensity. This is readily understood in terms of symmetry. Within the sudden approximation (monopole selection rules) SU transitions are only allowed if the initial and final states have the same symmetry. Figure 5 shows that within the  $C_{2v}$  character set of the neutral molecule the HOMO and LUMO levels have different symmetries,  $a_1(\pi)$  and  $b_2(\pi^*)$ , respectively. N1s and O1s ionization breaks the neutral molecule symmetry ( $C_{2v} \rightarrow C_s$ ), but does so along different axes (Fig. 6). In the broken symmetry, or localized core-hole solution, N1s ionization mixes orbitals of  $a_1$ and  $b_2$  symmetry and coupling with the HOMO  $\rightarrow$  LUMO excitation becomes allowed. HOMO  $\rightarrow$  LUMO excitation remains symmetry forbidden for O1s ionization.

In terms of ground state charge densities, SQ(H) can be viewed as two PNA molecules coupled end-to-end:  $D^+ - A^-: A^- - D^+$ . The orbitals best approximating the PNA intramolecular  $\pi^* \leftarrow \pi$  charge-transfer transition, however, are both doubly occupied in SQ(H) (the second HOMO and HOMO in Fig. 5). The O1s shake-up structure appears due in large part to localized carbonyl-type transitions. It is interesting that the SQ(H) O1s main peak binding energy, and the energies and intensities of the SU satellites do, in fact, parallel the O1s spectrum of *p*-benzoquinone [33].

It can easily be rationalized why enhanced intermolecular charge-transfer is normally expected for squaraine O1s ionization. The neutral solid chargetransfer transition is expected to occur from the donor dimethylamino group of one molecule, (HOMO (1st)) to the acceptor squaraine fragment of a second



Fig. 5. Schematic view from above the molecular plane of the initial and (Z + 1)-ionized SQ(H) orbitals of interest. The orbital lobes are drawn proportional to the LCAO coefficients. Symmetry-allowed ion-state transitions (SU) from the HOMO level are indicated by arrows.



Fig. 6. Mapping of the elements of the  $C_{2v}$  point group for neutral SQ(H) into the  $C_s$  reduced symmetry set induced by O1s and N1s ionization [56].

overlapping molecule (LUMO (2nd)) [5, 8]. This is suggested by the experimental structure and the orbitals of Fig. 5. Intermolecular charge-transfer in the neutral solid is already toward the center to be ionized — the O1s level of the second molecule. O1s ionization would stabilize LUMO (2nd), due to selective coulomb interactions, to more effectively draw intermolecular screening charge. The O1s SU feature reflecting this charge-transfer is thus expected to be shifted to a lower energy than the corresponding neutral solid transition. The O1s spectra deconvolutions of Figs. 1 and 2, and that for SQ(OCH<sub>3</sub>) in Fig. 3 are consistent with these arguments: the solid state intermolecular chargetransfer transition that appears at ~ 1.78 eV in the neutral system [8] is shifted to ~ 1.22 eV by O1s ionization. Figure 7 shows the relationship of the experimental XPS SU peaks to the optical absorption spectra of neutral SQ(H) in solution and in the solid.

The first N1s SU transition appears slightly above the neutral molecule solution phase absorption in Fig. 7. Due to selective coulomb interactions the N1s core-hole stabilizes the HOMO level more than the LUMO and shifts the excitation to slightly higher energy. This was found previously for dimethyl-amino-substituted organics [34]. It should also be emphasized that a neutral molecule ground state correlation was not included in the core-hole spectral intensity evaluations. It has been shown that the HOMO  $\rightarrow$  LUMO doubly-excited configuration, (61,61||62,62), contributes to  $|{}^{1}\Psi_{GS}(N)\rangle$  [13]. It is likely that such contributions would increase the intramolecular HOMO  $\rightarrow$  LUMO SU intensity for N1s ionization [57] (Fig. 4).

The broad C1s spectrum of SQ(H) is compared with several charge-potential model spectra in Fig. 8. A value for k of 21.4 was developed in the original



Fig. 7. Comparison of the energy and character of the first SU transition accompanying N1s and O1s ionization of SQ(H) with solution and solid state absorption spectra of the neutral molecule. The energy of the neutral solid intermolecular charge-transfer transition is for SQ(OH) [8].

charge-potential model for CNDO/2 charges [58]. Comparison of CNDO/2 [44] and CNDO/S [59] results for PBQ for example, shows that the CNDO/S method yields a greater  $C^{\delta_+}-O^{\delta_-}$  charge polarization. A smaller k is thus needed to reflect binding energy spreads as a function of atomic charge differences. A value for k of 11.0 was selected by fitting the C1s binding energy differences of PBQ ( $\Delta BE \simeq 3.0 \text{ eV}$  [33]) with previous CNDO/S results [59]. The chemical shifts within the highly polarized monomer units appear sufficient to rationalize the intense symmetric main peak centered at 285.0 eV, as well as the asymmetry on the high binding energy side. No attempt was made to include relaxation effects which could reorder relative ionization energies. Ionization of the carbons in the squaraine fragment, positions 1 and 2 in Fig. 8, may induce intermolecular charge-transfer SU satellites as was argued for O1s ionization. The intensity of these features, however, would be relatively weak when compared to the total C1s contribution.

## SUMMARY AND CONCLUSIONS

The solid-state N1s and O1s core-hole spectra of a series of highly polar squaraine molecules were analyzed in terms of intra- and inter-molecular contributions and related to corresponding excitations in the neutral solid. Specifically, it was argued that O1s ionization enhanced the donor (dimethylamino) to acceptor (squaraine fragment) intermolecular charge-transfer previously identified in neutral solid optical absorption studies. Intermolecular



Fig. 8. The C1s spectrum of SQ(H)-E. The CNDO/S neutral molecular ground state net atomic charges are given (300  $\times$  300 CI). The lines in the bottom panel reflect the binding energy spread of the different carbon environments obtained using a simple charge-potential model,  $\Delta BE_i = k\Delta q_i + \Delta q_i/r_y$ , with k = 21.4 [58] and assuming only nearest neighbor interactions. The relative heights reflect the atom degeneracies. The distribution in the top panel was calculated using k = 11.0 (see text).

charge-transfer was reflected in the O1s spectra as a relatively strong lowenergy satellite. This interpretation was supported by the results of a CNDO/S (CI) equivalent-core calculation which indicated an absence of low-lying satellites in the O1s monomer spectrum. The HOMO  $\rightarrow$  LUMO transition which usually leads to intense satellites accompanying acceptor ionization of organic D<sup>+</sup>-Ar-A<sup>-</sup> systems was shown to be symmetry forbidden for the O1s ionization of the parent squaraine monomer. The intermolecular charge-transfer excitation was absent in the O1s spectrum of SQ(OH). This was attributed to intramolecular hydrogen bonding interactions which probably provides a more energetically favorable pathway to core-hole screening.

O1s spectral deconvolutions were complicated by the presence of large amounts of "excess" or adsorbed oxygen. The concentration of adsorbed oxygen varied over a wide range for the squaraines studied. Differences in the O1s spectra of the seven squaraines studied were reflected by variations in the intensity of a single peak (BE  $\sim 533.0 \text{ eV}$ ) containing the percentage of "excess" oxygen. Comparisons of the two preparations of SQ(H) showed that the material with the greater "excess" oxygen exhibited a greater electrical conductivity.

N1s ionization produced satellite features which were nearly constant in energy and intensity throughout the series. The main features of the typical spectrum were reproduced by the equivalent-core model, although the calculated shake-up intensities were generally too weak. There was no clear evidence that satellite intensities were enhanced by intermolecular chargetransfer as was found for O1s ionization.

The broad asymmetric C1s profile characteristic of all the squaraines was attributed to a spread of chemically shifted carbons reflecting the highly charge polarized monomer units.

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