Visualizing the Contributions of Virtual States to Two-Photon Absorption Cross-Sections by Natural Transition Orbitals of Response Transition Density Matrices: Supporting Information

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1. NATURAL TRANSITION ORBITALS FOR ONE-PARTICLE TRANSITION DENSITY MATRIX

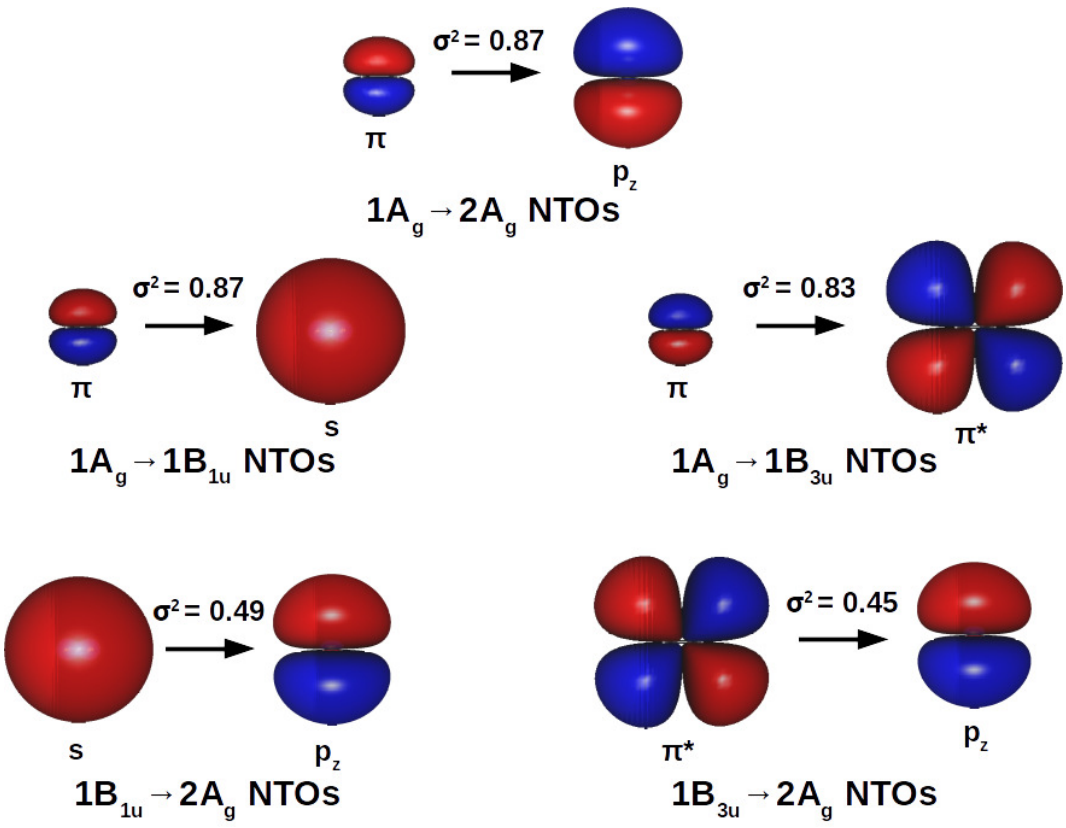

FIG. S1: Dominant NTOs (isovalue = 0.003) for various 1PA transitions in ethylene (*hole* → *particle* NTOs).

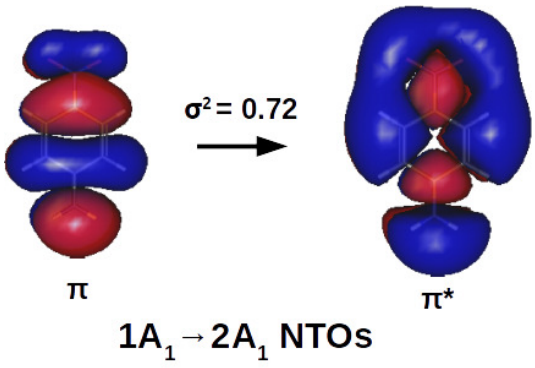

FIG. S2: Dominant NTOs (isovalue = 0.005) for various 1PA transitions in *para*-nitroaniline (*hole* → *particle* NTOs).

2. NATURAL TRANSITION ORBITALS FOR $f \to i$ ω DENSITY MATRICES

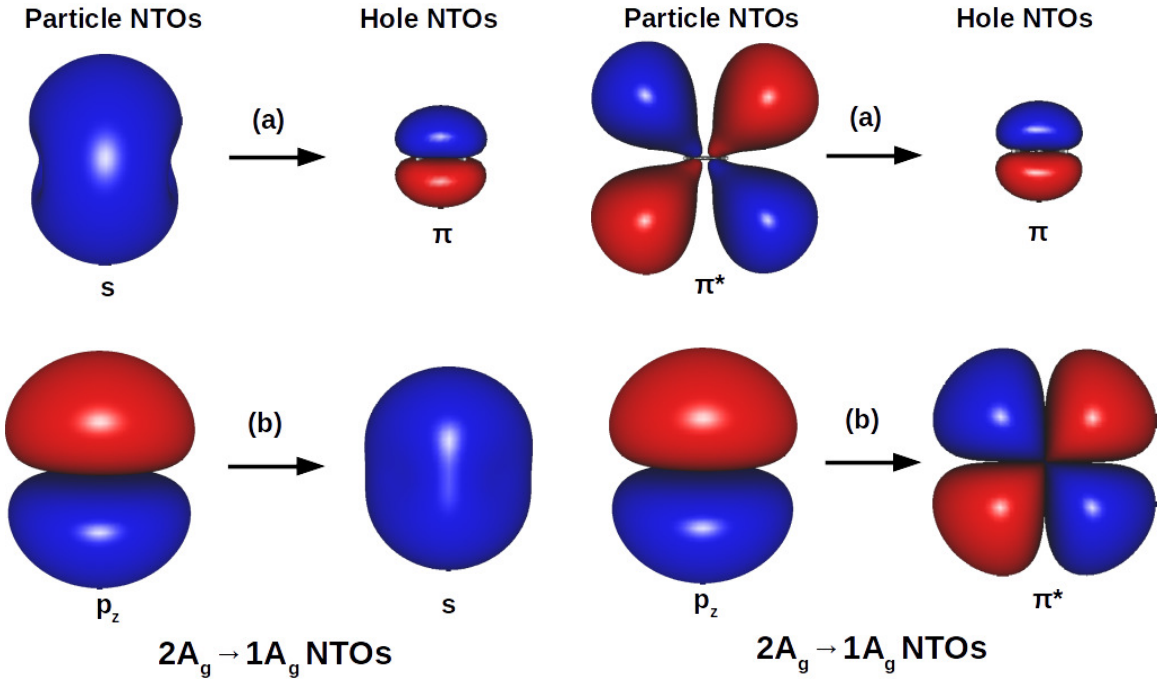

FIG. S3: Dominant NTOs (isovalue = 0.003) for the M_{zz} (left) and M_{xx} (right) 2PA transition moments for the $2A_g \to 1A_g$ ωDMs (ethylene, $\omega_1 = \omega_2 = 33911$ cm^{-1}).

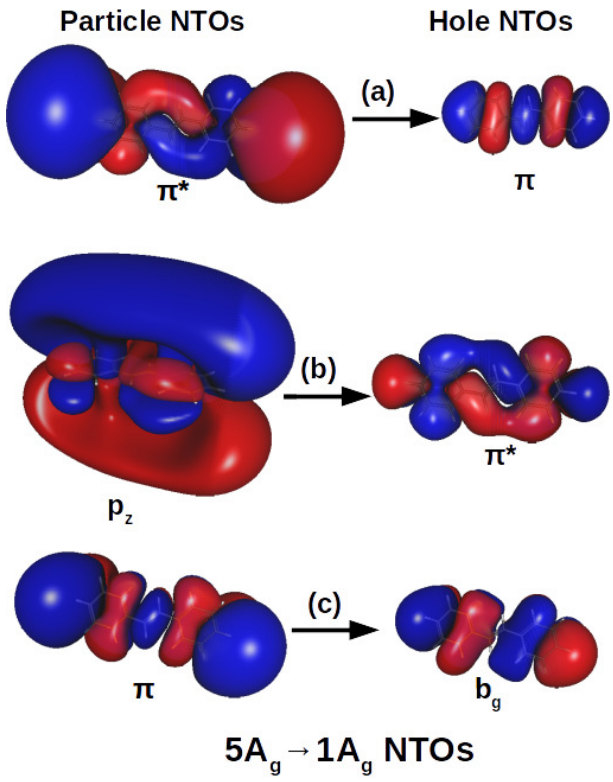

FIG. S4: Dominant NTOs (isovalue = 0.003) for the x-components of the ωDMs for the $5A_g \rightarrow 1A_g$ transition (*trans*-stilbene, degenerate photons).

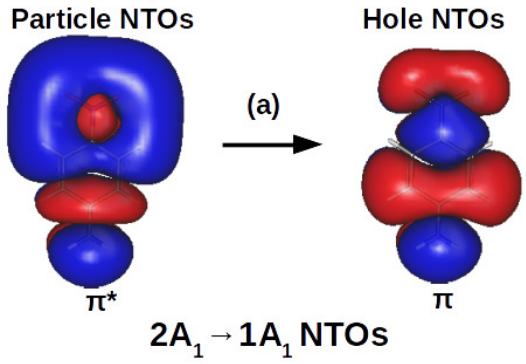

FIG. S5: Dominant NTOs (isovalue = 0.005) for the z-components of the ωDM for the $2A_1 \rightarrow 1A_1$ 2PA transition (pNA, degenerate photons).

3. PARTICIPATION RATIOS FOR NTOS OF PARTIAL ωDMS

TABLE S1: PR_{NTO} of partial ωDMs for 2PA transitions in ethylene and *trans*-stilbene.

ωDM component	Transition $i \to f$	$PR_{NTO}^{f \leftarrow X_i}$	$PR_{NTO}^{\tilde{X}_f \leftarrow i}$
Ethylene, $\omega_1 = \omega_2 = 33911$ cm^{-1}			
z	$1A_g \to 2A_g$	1.03	1.00
	$2A_g \to 1A_g$	1.00	1.03
x	$1A_g \to 2A_g$	1.01	1.00
	$2A_g \to 1A_g$	1.00	1.01
Ethylene, $\omega_1 = 63000$ cm^{-1}, $\omega_2 = 4821$ cm^{-1}			
x	$1A_g \to 2A_g$	1.01	1.00
	$2A_g \to 1A_g$	1.09	1.01
Ethylene, $\omega_1 = 4821$ cm^{-1}, $\omega_2 = 63000$ cm^{-1}			
x	$1A_g \to 2A_g$	1.02	1.09
	$2A_g \to 1A_g$	1.00	1.01
trans-Stilbene, ω_1=ω_2=25400 cm^{-1}			
x	$1A_g \to 2A_g$	1.98	1.06
	$2A_g \to 1A_g$	1.06	1.92

4. ANALYSIS OF THE 1PA AND 2PA EXCITONS IN ETHYLENE

TABLE S2: RMS hole-electron separations (d_{exc}) of x-component ωDMs for 2PA $1A_g \rightarrow 2A_g$ transitions in ethylene.

Transition	ω_1 (cm^{-1})	DM	d_{exc} (Å)	DM	d_{exc} (Å)
2PA $i \rightarrow f$		$\gamma_{+\omega_1}^{f\leftarrow X_i}$		$\gamma_{+\omega_1}^{f\leftarrow i}$	
	4821		5.10		3.13
	33911		5.13		5.75
	63000		5.30		5.27
1PA $1B_{3u} \rightarrow 2A_g$	63890	$\gamma_{1PA}^{2A_g\leftarrow 1B_{3u}}$	5.33		
2PA $f \rightarrow i$		$\gamma_{-\omega_2}^{i\leftarrow X_f}$		$\gamma_{-\omega_2}^{i\leftarrow f}$	
	4821		6.06		5.28
	33911		5.98		5.76
	63000		3.12		3.11
1PA $1B_{3u} \rightarrow 1A_g$	63890	$\gamma_{1PA}^{1A_g\leftarrow 1B_{3u}}$	2.68		

Table S2 presents the analysis of the average separation between the hole and electron for 2PA and 1PA NTOs as quantified by the RMS hole-electron separation, see Eq. (4) of the main manuscript. Table S2 shows that d_{exc} for the x-component partial transition ωDMs, $\gamma^{f\leftarrow X_i}$ and $\gamma^{i\leftarrow X_f}$, for $i \rightarrow f$ and $f \rightarrow i$ transitions depends on ω_1/ω_2. As one of the frequencies approaches the $1B_{3u}$-$1A_g$ transition frequency, d_{exc} for the 2PA transitions approach d_{exc} for the 1PA transitions $1B_{3u} \rightarrow 2A_g$ and $1B_{3u} \rightarrow 1A_g$. This reflects the change in the 2PA regime — as one approaches the resonant condition, the 2PA transition becomes increasingly more like the two 1PA transitions via the third state. We also provide these values for the full ωDMs. For non-degenerate 2PA cases, the d_{exc} values for $i \rightarrow f$ and $f \rightarrow i$ transitions are not the same for the same reason that the NTOs (a) and (b) dominate one or the other of these transitions in Table III of the Letter (related to the choice of ω_1 and ω_2). When ω_1 and ω_2 are swapped, the d_{exc} for the full ωDMs of $i \rightarrow f$ and $f \rightarrow i$ transitions are also swapped. Note that both photons are absorbed simultaneously, so the dissimilar d_{exc} for $i \rightarrow f$ and $f \rightarrow i$ transitions in the non-degenerate case is just a consequence of making the choice of ω_1 (the photon that is absorbed first from the vantage of theory). However, when both the $i \rightarrow f$ and $f \rightarrow i$ 2PA transitions are analyzed together, no information is lost and an estimate of the size of the "real" exciton can be deduced from the exciton sizes of individual $i \rightarrow f$ and $f \rightarrow i$ transitions.

5. RELEVANT CARTESIAN GEOMETRIES

5.1. Ethylene

```
C       0.6739740010     0.0000000004     0.0000000000
H       1.2458930051     0.9327300497    -0.0000000000
H       1.2458930051    -0.9327300497     0.0000000000
C      -0.6739739990     0.0000000009    -0.0000000000
H      -1.2458930031    -0.9327300485    -0.0000000000
H      -1.2458930024     0.9327300505    -0.0000000000
Nuclear repulsion energy = 33.0229346930 hartrees
```

5.2. *trans*-Stilbene

```
C       1.9336796415     0.1867437173    -0.0000000000
C       2.8205615161     1.2724153256    -0.0000000000
H       2.4196963848     2.2785315176    -0.0000000000
C       4.1956916641     1.0827452905    -0.0000000000
H       4.8558537337     1.9400950102    -0.0000000000
C       4.7221215333    -0.2025414579     0.0000000000
H       5.7929251583    -0.3551735773     0.0000000000
C       3.8567234950    -1.2940306139     0.0000000000
H       4.2563039951    -2.2997452666     0.0000000000
C       2.4849461081    -1.1037464882     0.0000000000
H       1.8353237326    -1.9679439024     0.0000000000
C       0.4957319183     0.4521168851    -0.0000000000
H       0.2395292512     1.5062120042    -0.0000000000
C      -0.4957319183    -0.4521168851     0.0000000000
H      -0.2395292512    -1.5062120042     0.0000000000
C      -1.9336796415    -0.1867437173     0.0000000000
C      -2.8205615161    -1.2724153256     0.0000000000
H      -2.4196963848    -2.2785315176     0.0000000000
C      -4.1956916641    -1.0827452905     0.0000000000
H      -4.8558537337    -1.9400950102     0.0000000000
C      -4.7221215333     0.2025414579    -0.0000000000
H      -5.7929251583     0.3551735773    -0.0000000000
C      -3.8567234950     1.2940306139    -0.0000000000
H      -4.2563039951     2.2997452666    -0.0000000000
C      -2.4849461081     1.1037464882    -0.0000000000
H      -1.8353237326     1.9679439024    -0.0000000000
Nuclear repulsion energy = 733.3969332446 hartrees
```

5.3. *para*-Nitroaniline

```
C       0.0000000000     0.0000000000     0.7153356937
C       1.2195927633     0.0000000000     0.0255507248
```

```
C       1.2182354930     0.0000000000    -1.3699791187
C       0.0000000000     0.0000000000    -2.0937199737
C      -1.2182354930     0.0000000000    -1.3699791187
C      -1.2195927633     0.0000000000     0.0255507248
H       2.1553754221     0.0000000000     0.5869226624
H       2.1689860113     0.0000000000    -1.9130375835
H      -2.1689860113     0.0000000000    -1.9130375835
H      -2.1553754221     0.0000000000     0.5869226624
N       0.0000000000     0.0000000000    -3.4666053646
N       0.0000000000     0.0000000000     2.1848883212
O      -1.0841264669     0.0000000000     2.7496493313
O       1.0841264669     0.0000000000     2.7496493313
H      -0.8656098383     0.0000000000    -3.9833468735
H       0.8656098383     0.0000000000    -3.9833468735
Nuclear repulsion energy = 493.6591981965 hartrees
```