**Supplementary Material for “THE VACUUM UV PHOTOABSORPTION SPECTROSCOPY OF** **THE TRANS-DICHLOROETHYLENE (1,2-ClHC=CClH) IN THE 5- 20 eV RANGE.EXPERIMENT AND THEORY.”**

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**TABLE S1** **:** Optimized geometry for the fundamental and of several excited

electronic states of trans-1,2-C2H2Cl2 neutral molecule in the C2h

symmetry point group. The geometry of the first 11Bu electronic

excited state is also optimized in the C2 symmetry point group.

The internuclear distances are in Ǻ and bond angles in degrees.

**TABLE S2:** Computed vibrational wavenumbers (cm-1) of the twelve normal

modes (V.n.M) of the neutral ground and first excited states of trans-

1,2-C2H2Cl2 in the C2h and C2 symmetry point group at the M06-2X and

TDDFT levels. The theoretical wavenumbers for the neutral ground

state are compared with experimental data [33]. Imaginary

wavenumbers are bold printed.

**TABLE S3:** Energy position (eV/cm-1), assignments and averaged energy/

wavenumbers (Avgd.En./Wavenbr.) of the structures observed in

the VUV PAS of trans-1,2-C2H2Cl2 between 8.26 eV and 9.14 eV.Com-

parison is made with earlier data [1, 2, 4]. Conversion factor 1eV=

8065.545 cm-1[19].

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electronic states of trans-1,2-C2H2Cl2 neutral molecule in the C2h

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|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **In C2h Symmetry** | | | | | |
| Level | C=C | C-Cl | C-H | H-C-C | Cl-C-C |
| **1Ag** | | | | | |
| CCSD | 1.3417 | 1.7467 | 1.0916 | 124.05 | 121.08 |
| M06-2X | 1.3271 | 1.7342 | 1.0871 | 124.12 | 121.11 |
| [30] | 1.314 | 1.736 | 1.079 | 123.89 | 121.49 |
| [31] | 1.331 | 1.733 | 1.083 | 123.8 | 121.2 |
| [32] | 1.322 | 1.730 | 1.079 | 123.8 | 121.8 |
| Expa | 1.332 | 1.725 | 1.092 | 124.00 | 120.83 |
| **11Bu (→\*b** | | | | | |
| CCSD | **1.5221** | 1.7158 | 1.0883 | 124.38 | **116.51** |
| M06-2X | **1.4853** | 1.6867 | 1.0834 | 124.93 | **115.74** |
| TDDFT | **1.4562** | 1.6856 | 1.0849 | 126.19 | **114.01** |
| **31Au (→Rs)** | | | | | |
| TDDFT | **1.3936** | **1.6599** | 1.089 | 122.72 | 120.11 |
| **51Au(→R[d+s+p])** | | | | | |
| TDDFT | **1.389** | 1.7553 | 1.0963 | **120.77** | **114.65** |
| **91Bu(nCl+σCC→Rpxy1)d** | | | | | |
| TDDFT | **-** | **-** | - | **-** | **-** |

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **In** **C2 Symmetry.** | | | | | |
| **11Bu/1B(C2)b** | | | | | |
|  | C=C | C-Cl | C-H | H-C-C | Cl-C-C |
| M06-2X  TDDFT | 1.3903 | 1.7509 | 1.0898 | 126.77 | 120.68 |
| 1.431 | 1.7551 | 1.0928 | 124.77 | 120.27 |
|  | H3-C1-C2-H5 | Cl4-C1-C2-Cl6 | Cl4-C1-C2-H5 | Cl4-C1-C2-H3 |  |
| M06-2X | -99.99 | -83.21 | 88.39 | -171.61 |  |
| TDDFT | -111.09 | -80.29 | 84.31 | -164.6 |  |

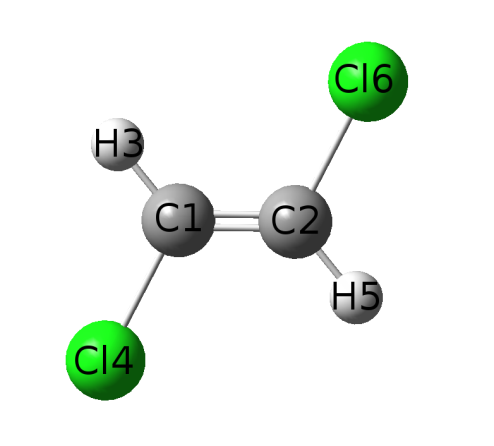
a Schäfer L., Ewbank J.D., Siam K., Paul D., Monts D.L., J.Mol.Struct. **145** (1986) 135.

b For details: see text.

c Vertical excitation energies calculated at the TDDFT level.

d This state could not be optimized owing to the large number of states in this energy

region.

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**TABLE S2:** Computed vibrational wavenumbers (cm-1) of the twelve normal

Modes (V.n.M) of the neutral ground and first excited states of trans-1,2-C2H2Cl2 in the C2h and C2 symmetry point group at the M06-2X and TDDFT levels. The theoretical wavenumbers for the neutral ground are compared with experimental data [33]. Imaginary wavenumbers are bold printed.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| States | **1Ag(C2h)** | | **11Bu** | | |
| V.n.M | Exp [33] | M06-2X | M06-2X | | TDDFT |
| ag/a |  |  | C2h | C2 | C2h |
| ν1 | 3073 | 3278 | 3281 | 3201 | 3286 |
| ν2 | 1578 | 1690 | 1369 | 1355 | 1327 |
| ν3 | 1274 | 1295 | 1183 | 1192 | 1170 |
| ν4 | 846 | 857 | 905 | 747 | 904 |
| ν5 | 350 | 358 | 322 | 120 | 332 |
| au/a |  |  |  |  |  |
| ν6 | 900 | 953 | **i195** | 520 | **i262** |
| ν7 | 227 | 202 | **i601** | 357 | i**718** |
| bg/b |  |  |  |  |  |
| ν8 | 763 | 828 | **i378** | 507 | **i482** |
| bu/b |  |  |  |  |  |
| ν9 | 3090 | 3272 | 3279 | 3193 | 3287 |
| ν10 | 1200 | 1217 | 1179 | 1168 | 1164 |
| ν11 | 828 | 841 | 898 | 736 | 900 |
| ν12 | 250 | 243 | 224 | 351 | 225 |

**TABLE S3:** Energy position (eV/cm-1), assignments and averaged energy /

wavenumbers (Avgd.En./Wavenbr.) of the structures observed in

the VUV PAS of trans-1,2-C2H2Cl2 between 8.26 eV and 9.14 eV.Com-

parison is made with earlier data [1, 2, 4]. Conversion factor 1eV=

8065.545 cm-1[19].

**(a)**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Rydb.Trans.au(π)]-1→4s; [δ=0.844]** | | | | | | |
| eV | cm-1 | [1] | [2] | [4] | Assign | Avgd.En./Wavenbr. |
| 8.267 | 66678 | 66674 |  |  | **4s(0,0)** | **→4s** |
| 8.312 | 67041 |  |  | 67071 | **ν5** | ω2=0.177±0.003 eV |
| 8.359 | 67420 |  |  | 67433 | 2ν5 | 1428±24 cm-1 |
| 8.390 | 67670 |  |  |  | **ν4** | ω3=0.160 eV |
| 8.402 | 67767 |  | 67770 |  | 3ν5 | 1290 cm-1 |
| 8.427 | 67928 |  |  |  | **ν3** | ω4=0.115±0.008 eV |
| 8.435 | 68033 |  |  |  | ν4+ν5 | 928±60 cm-1 |
| 8.441 | 68083 |  |  |  | **ν2/**4ν5 | ω5=0.044±0.004 eV |
| 8.474 | 68347 |  |  |  | ν4+2ν5 | 355±30 cm-1 |
| 8.485 | 68436 |  |  |  | ν2+ν5 |  |
| 8.490 | 68476 | 68486 |  | 68491 | 5ν5 |  |
| 8.496 | 68425 | 68538 |  |  | 2ν4 |  |
| 8.534 | 68831 |  |  | 68870 | ν2+2ν5 |  |
| 8.561 | 69049 | 69020 |  |  | ν2+ν4 |  |
| 8.579 | 69194 | 69249 | 69223 | 69215 | ν2+3ν5 |  |
| 8.606 | 69412 |  |  | 69407 | ν2+ν3 |  |
| 8.621 | 69533 |  |  |  | **2ν2** |  |
| 8.652 | 69783 |  |  |  | 2ν4+2ν5 |  |

**(b)**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Rydb.Trans. [2au()]-1→4d,4f (δ=0.053, 0.011)** | | | | |
| eV | cm-1 | Assignments | | Avg.En./Wavenbr. |
| 8.760 | 70654 | **(0,0)4d** |  | **4d-Rydb (δ=0.053)** |
| 8.779 | 70807 |  | **(0,0)4f** | ω12=30±3 meV |
| 8.793 | 70920 | **ν12** |  | 242±24 cm-1 |
| 8.799 | 70969 | na | na | ω5=43±3meV |
| 8.801 | 70985 | **ν5** |  | 347±24 cm-1 |
| 8.807 | 71033 |  | **ν12** | ω4=119 meV |
| 8.814 | 71090 | na | na | 960 cm-1 |
| 8.819 | 71130 | **2ν12** |  | ω3=164 meV |
| 8.823 | 71162 |  | **ν5** | 1323 cm-1 |
| 8.838 | 71283 |  | **2ν12** | ω2=176 meV |
| 8.853 | 71404 | **2ν5** |  | 1419 cm-1 |
| 8.858 | 71445 | na | na |  |
| 8.869 | 71533 |  | **2ν**5 | **4f-Rydb (δ=0.009)** |
| 8.879 | 71614 | **ν4** |  | ω12=29±1 meV |
| 8.891 | 71711 | **3ν5** |  | 234±8 cm-1 |
| 8.895 | 71743 |  | **ν4** | ω5=44±1 meV |
| 8.898 | 71767 |  | 2ν5+ν12 | 355±8 cm-1 |
| 8.906 | 71832 | ν4+ν5 |  | ω4=117±5 meV |
| 8.916 | 71912 |  | **3ν5** | 944±40 cm-1 |
| [8.924] | 71977 | **ν3** | ν4+ν12 | ω3=160±2 meV |
| [8.936] | 72074 | **ν2** | **ν3** | 1290±16 cm-1 |
| 8.941 | 72114 |  | ν4+ν5 | ω2=180±2 meV |
| 8.953 | 72211 | ν3+ν5 |  | 1452±16 cm-1 |
| 8.958 | 72251 |  | **ν2** |  |
| 8.966 | 72316 | ν2+ν12 |  |  |
| 8.971 | 72356 | ν2+ν5 |  |  |
| 8.983 | 72453 |  | ν4+2ν5 |  |
|  |  |  | ν3+ν5 |  |
| 8.993 | 72533 |  |  |  |
| 9.002 | 72606 |  |  |  |
| 9.015 | 72711 |  | **2ν4** |  |
| 9.029 | 72824 |  | ν4+3ν5 |  |
| 9.035 | 72872 |  | na |  |
| 9.051 | 73001 |  | na |  |
| 9.057 | 73050 |  | na |  |
| 9.075 | 73195 |  | ν3+2ν5 |  |
| 9.087 | 73292 |  | na |  |
| 9.101 | 73404 |  | **2ν3** |  |
| 9.113 | 73501 |  | na |  |
| 9.121 | 73566 |  | ν2+ν3 |  |
| 9.135 | 73679 |  | **2ν2** |  |