Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

Resonant Two-Photon Photoelectron Imaging and Adiabatic Detachment Processes from Bound Vibrational Levels of Dipole-Bound States

Dao-Fu Yuan, Yue-Rou Zhang, Chen-Hui Qian and Lai-Sheng Wang*

Department of Chemistry, Brown University, Providence, Rhode Island 02912, USA

*Email: Lai-Sheng_Wang@brown.edu

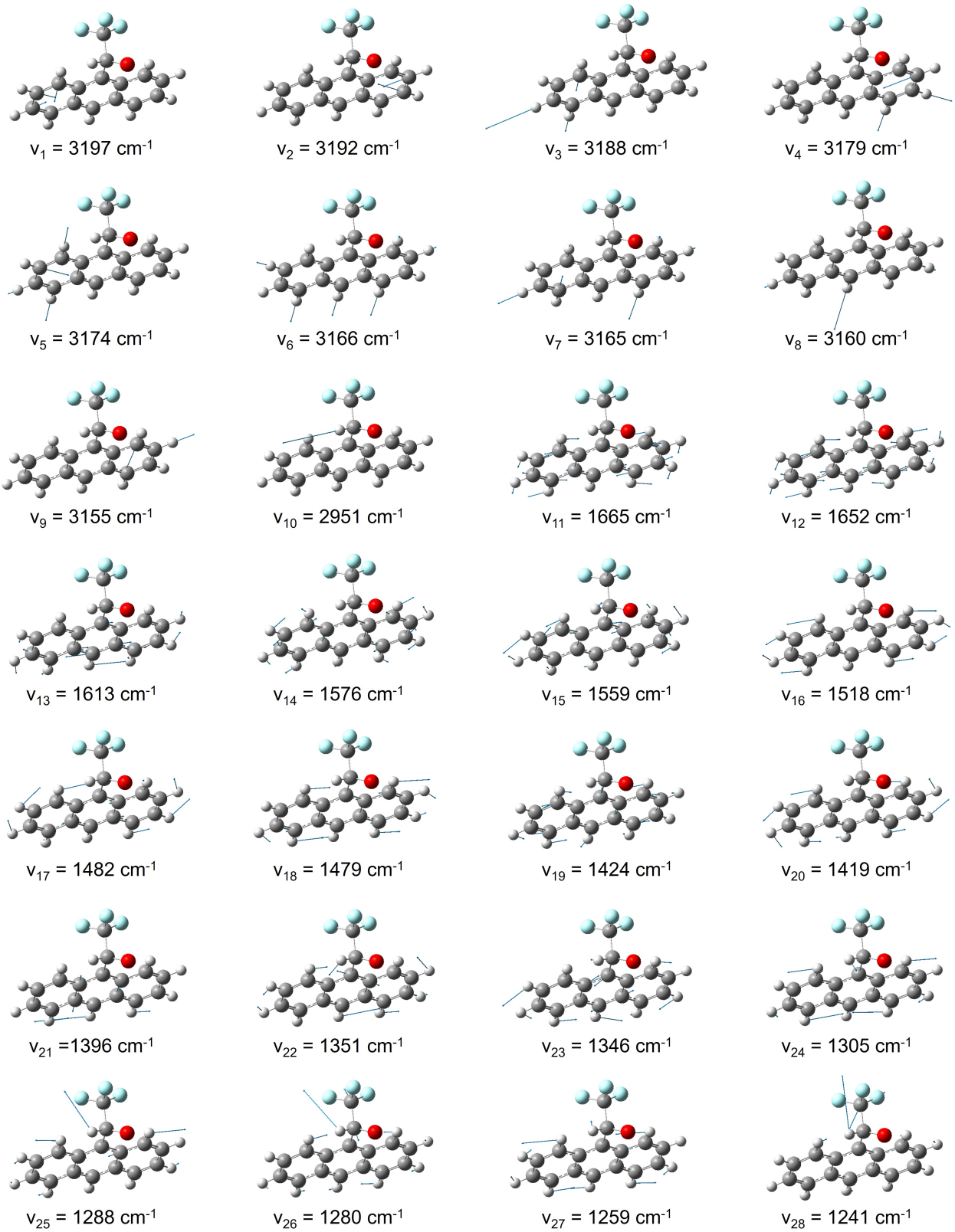

Fig. S1 continued

Fig. S1 continued

Fig. S1. The atomic displacement vectors of the vibrational modes for *R*-TFAE. The computed frequencies are also shown.

Table S1. The measured adiabatic detachment energies (ADE) of the photoelectron bands of *R*-TFAE$^-$ and the excitation energies (ΔE) of the excited state of neutral *R*-TFAE, compared with the calculated excitation energy.

Observed feature	ADE (eV) (exp)	ΔE (eV) (exp)	ΔE (eV) (theo. vert) [a]	ΔE (eV) (theo. adia) [b]
$\tilde{X}$	2.5234 (2)	\	\	\
$\tilde{A}$	2.72 (2)	0.20	0.54	0.32

[a]Calculated using the optimized geometry of the neutral ground state (vertical excitation).

[b]Calculated using the optimized geometry of corresponding excited state (adiabatic excitation).

Table S2. The theoretical frequencies of *R*-TFAE at the DFT/ B3LYP/6-311++ (d, p) level of theory.

Mode	Frequency(cm^{-1})	Mode	Frequency(cm^{-1})	Mode	Frequency(cm^{-1})
ν_1	3197	ν_{29}	1218	ν_{57}	702
ν_2	3192	ν_{30}	1207	ν_{58}	657
ν_3	3188	ν_{31}	1183	ν_{59}	637
ν_4	3179	ν_{32}	1178	ν_{60}	630
ν_5	3174	ν_{33}	1157	ν_{61}	611
ν_6	3166	ν_{34}	1130	ν_{62}	565
ν_7	3165	ν_{35}	1125	ν_{63}	552
ν_8	3160	ν_{36}	1121	ν_{64}	530
ν_9	3155	ν_{37}	1087	ν_{65}	505
ν_{10}	2951	ν_{38}	1044	ν_{66}	499
ν_{11}	1665	ν_{39}	1040	ν_{67}	475
ν_{12}	1652	ν_{40}	1013	ν_{68}	445
ν_{13}	1613	ν_{41}	991	ν_{69}	415
ν_{14}	1576	ν_{42}	989	ν_{70}	401
ν_{15}	1559	ν_{43}	972	ν_{71}	401
ν_{16}	1518	ν_{44}	969	ν_{72}	321
ν_{17}	1482	ν_{45}	933	ν_{73}	307
ν_{18}	1479	ν_{46}	912	ν_{74}	275
ν_{19}	1424	ν_{47}	879	ν_{75}	237
ν_{20}	1419	ν_{48}	863	ν_{76}	229
ν_{21}	1396	ν_{49}	855	ν_{77}	224
ν_{22}	1351	ν_{50}	845	ν_{78}	200
ν_{23}	1346	ν_{51}	823	ν_{79}	162
ν_{24}	1305	ν_{52}	782	ν_{80}	111
ν_{25}	1288	ν_{53}	763	ν_{81}	85
ν_{26}	1280	ν_{54}	741	ν_{82}	54
ν_{27}	1259	ν_{55}	739	ν_{83}	45
ν_{28}	1241	ν_{56}	718	ν_{84}	38

Table S3. The calculated excitation energies (ΔE) of the excited states of *R*-TFAE^{-}.

Excited States	Multiplicity	ΔE (eV) (theo. vert.) [a]
1	Triplet	1.39
2	Singlet	1.50
3	Triplet	1.73
4	Singlet	1.78
5	Triplet	1.83
6	Triplet	2.68

[a]Calculated from the time-dependent density functional theory using the optimized geometry of the neutral ground state.