Supporting Information: The Electronic Spectrum of the Tropylium Cation in the Gas Phase

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S1 Methods

S1.1 Theoretical methods and results

The necessary input files, in order to replicate the calculations described in this work, are given in section 1.2.4.

S1.1.1 Geometries and binding energies for Tr^+, Tr^+-Ar and Bz^+

Geometries and harmonic zero-point energies for Tr^+, the Tr^+-Ar complexes, and Bz^+ were calculated at the DFT PW6B95-D3(BJ)/jul-cc-pVTZ level of theory.[1–3] The highest Abelian group symmetry was employed for the geometry optimizations. The electronic energies were refined with the DLPNO-CCSD(T) theory along with the aug-cc-pVQZ basis set.[4,5] The "Superfine" integration grid was employed for the DFT computations. The DFT and DLPNO-CCSD(T) calculations were performed using the Gaussian 16 and ORCA 4.1 packages, respectively.[6,7]

Table S1: Bond lengths for Tr^+ in the S_0 and S_1 electronic states obtained from geometry optimization at CASSCF(6,7)/def2-TZVP level of theory.

Bond	State	Length (Å)	State	Length (Å)
C-C	S_0	1.391	S_1	1.404
				1.415
				1.425
				1.428
				1.426
				1.417
				1.406
C-H	S_0	1.074	S_1	1.075
				1.074
				1.073
				1.072
				1.071
				1.072
				1.073

Table S2: Calculated vibrational frequencies in cm^{-1} for Tr^+ in the S_0 and S_1 states, determined at the CASSCF(6,7)/def2-TZVP level of theory. All vibrational frequencies are scaled by 0.915, a factor that gives the most satisfactory match between simulated and experimental spectra and which is comparable to the factor used for similar systems.[8] Each mode's symmetry is given for the D_{7h} point group with corresponding symmetry upon descent to C_s given in parentheses. 6 vibrational modes for the S_1 state (ν_5, ν_9, ν_{15}) could not be clearly correlated with S_0 state vibrations because of Duschinsky mixing.

Mode	Symmetry	Frequency S_0 state	Frequency S_1 state
ν_1	a_1' (a′)	3079	3083
ν_2	a_1' (a′)	827	785
ν_3	a_2' (a′)	1428	1400
ν_4	a_2'' (a″)	681	661
ν_5	e_1' (a′)	3075	NA/NA
ν_6	e_1' (a′)	1493	1441/1446
ν_7	e_1' (a′)	964	696/870
ν_8	e_1'' (a″)	872	734/766
ν_9	e_2' (a′)	3067	NA/NA
ν_{10}	e_2' (a′)	1593	1509/1528
ν_{11}	e_2' (a′)	1211	1120/1143
ν_{12}	e_2' (a′)	427	388/392
ν_{13}	e_2'' (a″)	1028	873/888
ν_{14}	e_2'' (a″)	266	212/212
ν_{15}	e_3' (a′)	3059	NA/NA
ν_{16}	e_3' (a′)	1511	1416/1433
ν_{17}	e_3' (a′)	1279	1247/1250
ν_{18}	e_3' (a′)	875	871/888
ν_{19}	e_3'' (a″)	1050	941/1010
ν_{20}	e_3'' (a″)	568	416/483

S1.1.2 Vertical excitation energy calculations

Vertical excitation energies were computed using the equation-of-motion coupled cluster (EOM-CC) approach[9] using the Gaussian 16 package.[6] The cluster expansion was limited to single and double excitations (i.e. EOM-CCSD). The lowest two roots, corresponding to the S_1 and S_2 states, were calculated using the aug-cc-pVTZ basis set.[5] The $1s$ electrons on carbon atoms were left uncorrelated. The excitation energies were calculated using the C_{2v} Abelian subgroup of the ground-state point group D_{7h}.

S1.1.3 Franck-Condon/Herzberg-Teller simulations for the $S_1 \leftarrow S_0$ spectrum of Tr^+

The FCHT simulations were performed using the time-dependent implementation of de Souza, Neese, and Iszák.[10]

The input geometries and Hessian matrices for the S_0 A_1' and S_1 E_3' states were calculated at the CASSCF(6,7)/def2-TZVP level of theory.[11,12] The active space was comprised of the full π-system, i.e. six electrons distributed within seven orbitals. The def2-TZVP basis set was employed along with the def2/JK auxiliary basis for the resolution of the identity approximation applied to the CASSCF integral transformation steps.[13] State-specific wavefunctions were computed for the S_0 and S_1 states. Optimizations were performed using analytical gradients, whereas the Hessian matrices were computed via finite differences of analytical gradients with steps of 0.005 Bohr. Initial guess orbitals were generated from a restricted Hartree-Fock wavefunction with the def2-SV(P) basis. No symmetry constraints were employed for any CASSCF calculations.

Damping functions were employed for the dual purposes of phenomenologically modelling broadening in the experimental spectrum and to assist convergence of computing the correlation function. Linewidths of $12\,cm^{-1}$ (Gaussian) and $100\,cm^{-1}$ (Lorentzian) were used to compute "stick" and broadened spectra, respectively. Delta functions or narrower linewidth (i.e. longer decay time) damping functions were not practicable due to poor convergence in the correlation function. Spectra were simulated at 0 K.

The lower (S_0) and upper state (S_1) geometries were superimposed to best satisfy the Eckart conditions and the normal modes were matched to take into account the Duschinsky rotation. The partial first derivatives of the transition dipole moment were calculated by finite differences with steps of 0.01 Bohr along the normal coordinates of the S_1 E_3' state. Finally, the frequencies of the simulated spectrum were scaled by 0.915 and blue-shifted by $\sim$ 2990 cm^{-1} to best match the experimental spectrum.

All CASSCF and Franck-Condon/Herzberg-Teller calculations were performed using the ORCA 4.1 program.[7]

S1.1.4 S_1 potential energy surface for Tr^+

Potential energy surfaces for the S_1 state were computed at the same CASSCF(6,7)/def2-TZVP level of theory as the Franck-Condon/Herzberg-Teller calculations, with the addition of the RIJK approximation using the def2/JK auxiliary basis.[13] The elec-

tronic energy was calculated as a function of the S_0 ν_2 and both degenerate components of the S_0 ν_7 normal coordinates starting from the ground state geometry (i.e. the Franck-Condon point). The scans were performed in dimensionless normal coordinates with a step size of 0.1 a.u. for both modes.

The state-averaged CASSCF wavefunction was computed including the S_0 state and both components of the S_1 state at each grid point, yielding the adiabatic potential energy surfaces shown in Figs. 4b and 5b.

S1.1.5 Jahn-Teller vibronic coupling calculations

In order to calculate the lowest vibronic levels and to estimate the impact of JT activity on the $S_1 \leftarrow S_0$ electronic spectrum, the vibronic wavefunctions are modelled following the approach of Longuet-Higgins and coworkers.[14,15] The vibronic wavefunctions are approximated as:

$$\Psi = \psi^+ e^{i\theta} + \psi^- e^{-i\theta} \tag{S1}$$

where ψ^+ and ψ^- represent the diabatic wavefunctions before JT interaction and θ is the angular coordinate of the electronic state. The model Hamiltonian is given by a two-dimensional harmonic oscillator:

$$\widehat{H}_0 = \frac{1}{2}\left(r^2 - \frac{\delta^2}{\delta r^2} - \frac{1}{r}\frac{\delta}{\delta r} - \frac{1}{r^2}\frac{\delta^2}{\delta \phi^2}\right) \tag{S2}$$

perturbed by a mixing operator:

$$\widehat{H}' = kr\left(e^{i(2\theta-\phi)} + e^{-i(2\theta-\phi)}\right) \tag{S3}$$

where r and ϕ are the polar vibrational coordinates in terms of the two degenerate normal modes. k is the dimensionless energy given by:

$$k^2 = \frac{2E_{\mathrm{JT}}}{E_{\mathrm{ZPE}}} \tag{S4}$$

where E_{JT} is the JT stabilization (see Fig. 5c in the paper) and E_{ZPE} is the zero-point energy of the uncoupled doubly-degenerate ω_{JT} (i.e. E_{ZPE} is 899 cm^{-1}). Together, these equations give an expression for the vibronic energy levels:

$$\begin{bmatrix} \widehat{H}_0 - E & kre^{-i\phi} \\ kre^{i\phi} & \widehat{H}_0 - E \end{bmatrix} \begin{bmatrix} \psi_l^+ \\ \psi_l^- \end{bmatrix} = 0. \tag{S5}$$

where the quantum number l indicates the vibrational angular momentum. Following Longuet-Higgins and coworkers,[14,15] the energy levels are numerically evaluated by expansion of $\psi_l^{+/-}$ in a basis of isotropic 2-dimensional harmonic oscillators. The final eigenvalue problem for a given value of l is given by:

$$\begin{bmatrix} l+1-E & k\sqrt{l+1} & 0 & 0 & \dots \\ k\sqrt{l+1} & l+2-E & k\sqrt{1} & 0 & \dots \\ 0 & k\sqrt{1} & l+3-E & k\sqrt{l+2} & 0 \\ 0 & 0 & k\sqrt{l+2} & l+4-E & \ddots \\ \vdots & \vdots & 0 & \ddots & \ddots \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \\ \vdots \end{bmatrix} = 0. \tag{S6}$$

Diagonalization of Equation S6 yields the vibronic energy levels for a given l in units of ω_{JT}. The only parameter in this model is k, which is calculated using Equation S4 using the values of E_{JT} (120 cm^{-1}) and ω_{JT} (899 cm^{-1}) extracted from the potential energy slices shown in Figure 5c in the manuscript. Diagonalization was performed with a basis of 1000 harmonic oscillator functions.

The energy levels are conveniently denoted by $|\upsilon_7, j\rangle$ where υ_7 is the number of quanta in the ν_7 mode, and $j = l \pm \Lambda/2$, where Λ is the quantum number associated with the projection of the total electronic angular momentum onto the principal axis. The S_1 excited state has $l = -\upsilon, \dots, -1, 0, 1, \dots, \upsilon$ and $\Lambda = 1$, giving $j = \pm 1/2, \pm 3/2, \dots$. The selection rule for transitions between JT-active vibronic levels is $\Delta j = \pm 1/2$. The $\upsilon_7 = 0$ level of the S_0 ground state has zero vibrational angular momentum ($l = 0$) and electronic angular momentum ($\Lambda = 0$), giving $j = 0$. Therefore, transitions to the S_1 $|\upsilon_7 \geq 0, \pm 1/2\rangle$ vibronic levels are allowed and contribute to the spectrum, whereas transitions to $j = \pm 3/2, \pm 5/2, \dots$ levels are forbidden.

The model of Longuet-Higgins and coworkers can be used to predict the intensities for transitions from the vibrationless level of the $^1A_1'$ ground state to the Jahn-Teller active vibrational levels of the $^1E_3'$ state.[14] Assuming equivalent harmonic vibrational frequencies in the S_1 and S_0 states, the intensities are given by the elementwise square of the eigenvectors from Equation S6.[14,16] Relative intensities for transitions to the three lowest $j = \pm 1/2$ levels are predicted to be 1.00, 0.21, and 0.01, respectively. In the case of dipole-allowed transitions for a range of other molecules it has been found that incorporating the intensities for the Jahn-Teller active modes from this model with the usual Franck-Condon intensities adequately reconstructs the experimental spectrum.[16,17]

Table S3: Jahn-Teller levels $|\upsilon_7, j\rangle$ for the ν_7 mode of Tr^+ in the S_1 state. Relative intensities of transitions to the $|\upsilon_7, 1/2\rangle$ levels from the S_0 A_1' ground state are also given.

level $\|\upsilon_7, j\rangle$	energy (cm^{-1})	relative intensity
$\|0, \pm 1/2\rangle$	805	1.0
$\|1, \pm 1/2\rangle$	1864	0.21
$\|2, \pm 1/2\rangle$	2650	0.013
$\|3, \pm 1/2\rangle$	3628	0.0007
$\|4, \pm 1/2\rangle$	4478	0.00002
$\|1, \pm 3/2\rangle$	1550	
$\|2, \pm 3/2\rangle$	2837	
$\|3, \pm 3/2\rangle$	3497	
$\|4, \pm 3/2\rangle$	4550	
$\|2, \pm 5/2\rangle$	2322	
$\|3, \pm 5/2\rangle$	3750	
$\|4, \pm 5/2\rangle$	4395	
$\|3, \pm 7/2\rangle$	3110	
$\|4, \pm 7/2\rangle$	4623	
$\|4, \pm 9/2\rangle$	3909	

S1.1.6 Input files for electronic structure calculations

DFT geometry optimization in Gaussian 16

`tr+.gjf` – optimization and frequencies for Tr^+

```
%nprocshared=4
%mem=6gb
%chk=tr.chk
# PW6B95D3/jul-cc-pVTZ opt=verytight freq int=superfine symm=loose

Tr+ optimization

1 1
  C   0.00000000000000      1.60969400000000      0.00000000000000
  C   1.25850900000000      1.00362800000000      0.00000000000000
  C   1.56933600000000     -0.35819100000000      0.00000000000000
  C   -1.25850900000000      1.00362800000000      0.00000000000000
  C   0.69842000000000     -1.45028400000000      0.00000000000000
  C   -1.56933600000000     -0.35819100000000      0.00000000000000
  C   -0.69842000000000     -1.45028400000000      0.00000000000000
  H   0.00000000000000      2.70350500000000      0.00000000000000
  H   2.11368500000000      1.68560800000000      0.00000000000000
  H   2.63572300000000     -0.60158600000000      0.00000000000000
  H   -2.11368500000000      1.68560800000000      0.00000000000000
  H   1.17300700000000     -2.43577400000000      0.00000000000000
  H   -2.63572300000000     -0.60158600000000      0.00000000000000
  H   -1.17300700000000     -2.43577400000000      0.00000000000000
```

`bz+.gjf` – optimization and frequencies for Bz^+

```
%nprocshared=4
%mem=6gb
%chk=bz.chk
# PW6B95D3/jul-cc-pVTZ opt=verytight freq int=superfine symm=loose

Bz+ optimization

1 1
  C   -0.00000175566265      0.00000079054017     -1.78802869360433
  C   0.00000431533994     -1.23504980154816     -1.11300608613805
  C   0.00000732664054     -1.24500470929033      0.26027109433406
  C   0.00000562232291     -0.00000051798108      0.98691547109653
  C   0.00000437457952      1.24500466248576      0.26027139264930
  C   0.00000377861726      1.23505149649189     -1.11300540990915
  H   -0.00001605139132     -0.00000035035932     -2.88230140536497
  H   0.00000116999314     -2.16604671832250     -1.68230562792884
  H   0.00000965308944     -2.18623906907334      0.81677400513843
  H   -0.00000389385993      2.18623899248934      0.81677339245910
  H   0.00000020819374      2.16604657087094     -1.68230840562489
  C   0.00002199991267     -0.00000050111777      2.35344563594351
  H   -0.00003759524512     -0.93553219366361      2.92325254463269
  H   0.00000084746986      0.93553134847802      2.92325209231663
```

`tr+-ar1.gjf` – optimization and frequencies for Tr^{+}-Ar1

```
%nprocshared=4
%mem=6GB
%chk=tr_ar1.chk
# opt=verytight freq geom=connectivity jul-cc-pVTZ int=superfine pw6b95d3
symm=loose

Tr+-Ar optimization

1 1
 C                  0.00000000    1.47185419    0.96566632
 C                 -1.15074194    0.91768608    0.96566632
 C                 -1.43495173   -0.32751837    0.96566632
 C                  1.15074194    0.91768608    0.96566632
 C                 -0.63861360   -1.32609480    0.96566632
 C                  1.43495173   -0.32751837    0.96566632
 C                  0.63861360   -1.32609480    0.96566632
 H                  0.00000000    2.52287635    1.17691296
 H                 -1.97246416    1.57298767    1.17691296
 H                 -2.45962257   -0.56139280    1.17691296
 H                  1.97246416    1.57298767    1.17691296
 H                 -1.09463502   -2.27303305    1.17691296
 H                  2.45962257   -0.56139280    1.17691296
 H                  1.09463502   -2.27303305    1.17691296
 Ar                -0.00000000    0.00000000   -1.89513027
 X                  0.00000000   -0.00000000    0.69247395

 1 2 1.5 4 1.5 8 1.0
 2 3 2.0 9 1.0
 3 5 2.0 10 1.0
 4 6 1.0 11 1.0
 5 7 1.5 12 1.0
 6 7 1.5 13 1.0
 7 14 1.0
 8
 9
 10
 11
 12
 13
 14
 15
```

`tr+-ar2.gjf` – optimization and frequencies for Tr^{+}-Ar2

```
%nprocshared=4
%mem=6GB
%chk=tr_ar2.chk
# opt=verytight freq geom=connectivity jul-cc-pVTZ int=superfine pw6b95d3
symm=loose

Tr+-Ar optimization

1 1
 C                  0.00000000    1.56297145   -0.93468371
 C                  0.00000000    0.69539354    0.15257595
 C                  0.00000000   -0.69539354    0.15257595
 C                  0.00000000    1.25281240   -2.29064328
 C                  0.00000000   -1.56297145   -0.93468371
 C                  0.00000000    0.00000000   -2.89449721
 C                  0.00000000   -1.25281240   -2.29064328
 H                  0.00000000    2.61006541   -0.69578991
 H                  0.00000000    1.16176427    1.12056270
 H                  0.00000000   -1.16176427    1.12056270
 H                  0.00000000    2.09287175   -2.96056887
 H                  0.00000000   -2.61006541   -0.69578991
 H                  0.00000000    0.00000000   -3.96842923
 H                  0.00000000   -2.09287175   -2.96056887
 Ar                 0.00000000    0.00000000    3.51514217

 1 2 1.5 4 1.5 8 1.0
 2 3 1.5 9 1.0
 3 5 1.5 10 1.0
 4 6 1.5 11 1.0
 5 7 1.5 12 1.0
 6 7 1.5 13 1.0
 7 14 1.0
 8
 9
 10
 11
 12
 13
 14
 15
```

`tr+-ar3.gjf` – optimization and frequencies for Tr^{+}-Ar3

```
%nprocshared=4
%mem=6GB
%chk=tr_ar3.chk
# opt=verytight freq geom=connectivity jul-cc-pVTZ int=superfine pw6b95d3
symm=loose

Tr+-Ar optimization

1 1
 C                  0.00000000    1.56298452    1.92648032
 C                  0.00000000    0.69539545    3.01373108
 C                  0.00000000   -0.69539545    3.01373108
 C                  0.00000000    1.25283939    0.57051757
 C                  0.00000000   -1.56298452    1.92648032
 C                  0.00000000    0.00000000   -0.03334922
 C                  0.00000000   -1.25283939    0.57051757
 H                  0.00000000    2.61007602    2.16538487
 H                  0.00000000    1.16175624    3.98172261
 H                  0.00000000   -1.16175624    3.98172261
 H                  0.00000000    2.09290561   -0.09939940
 H                  0.00000000   -2.61007602    2.16538487
 H                  0.00000000    0.00000000   -1.10728124
 H                  0.00000000   -2.09290561   -0.09939940
 Ar                 0.00000000    0.00000000   -4.27353848

 1 2 1.5 4 1.5 8 1.0
 2 3 1.5 9 1.0
 3 5 1.5 10 1.0
 4 6 1.5 11 1.0
 5 7 1.5 12 1.0
 6 7 1.5 13 1.0
 7 14 1.0
 8
 9
 10
 11
 12
 13
 14
 15
```

EOM-CCSD vertical excitation energies in Gaussian 16

```
%nprocshared=4
%mem=40gb
%oldchk=tr.chk
%chk=tr_eomccsd.chk
# eomccsd(nstpir=-1)/aug-cc-pVTZ geom=check guess=read

vee

1 1

2 0 2 0
```

DLPNO-CCSD(T) single-point energies in ORCA 4.1

`tr.inp` – tropylium cation

```
! DLPNO-CCSD(T) aug-cc-pVQZ aug-cc-pVQZ/C TightSCF

%pal nproc 4 end
%maxcore 3000

*xyzfile 1 1 tr.xyz
```

`tr.xyz`

```
14

C    -0.0000002611    1.5969606051    0.
C    1.2485538986    0.9956888631    0.
C    1.5569215068    -0.3553568859    0.
C    -1.2485542242    0.9956884548    0.
C    0.692895465    -1.4388116364    0.
C    -1.5569213906    -0.3553573949    0.
C    -0.6928949945    -1.438811863    0.
H    -0.0000004375    2.6762741975    0.
H    2.0923951346    1.6686300189    0.
H    2.6091744932    -0.5955265824    0.
H    -2.0923956801    1.6686293347    0.
H    1.1611922411    -2.4112395053    0.
H    -2.6091742985    -0.5955274356    0.
H    -1.1611914527    -2.4112398849    0.
```

bz.inp – benzylium cation

```
! DLPNO-CCSD(T) aug-cc-pVQZ aug-cc-pVQZ/C TightSCF

%pal nproc 4 end
%maxcore 3000

*xyzfile 1 1 bz.xyz
```

bz.xyz

```
14

C    0.0000001873    0.0000013109    -1.7760520842
C    0.0000078108    -1.2260369396    -1.1037772319
C    0.0000112764    -1.2357755503    0.2587633232
C    0.0000070945    -0.0000004901    0.9770066722
C    -0.0000006915    1.2357755099    0.25876494
C    -0.0000040628    1.2260386818    -1.1037756279
H    -0.0000025198    0.0000020167    -2.8550817025
H    0.0000108556    -2.1450461097    -1.6639091652
H    0.0000171452    -2.1610828767    0.812093725
H    -0.0000037838    2.1610821123    0.8120965524
H    -0.0000099182    2.1450485847    -1.6639063587
C    0.0000105018    -0.0000013785    2.3351068095
H    0.0000163752    -0.9221677611    2.8963409863
H    0.0000074445    0.9221642699    2.8963421928
```

ar.inp – argon atom

```
! DLPNO-CCSD(T) aug-cc-pVQZ aug-cc-pVQZ/C TightSCF

%pal nproc 4 end
%maxcore 3000

*xyzfile 0 1 ar.xyz
```

ar.xyz

```
1

Ar     0.    0.0000000007    0.000
```

ar1.inp – first Tr^+-Ar complex

```
! DLPNO-CCSD(T) aug-cc-pVQZ aug-cc-pVQZ/C TightSCF

%pal nproc 4 end
%maxcore 3000

*xyzfile 1 1 ar1.xyz
```

ar1.xyz

```
15

C     -0.0000000021    1.5968407893    1.1072716438
C     -1.2484604023    0.995613946    1.1072716438
C     -1.5568046556    -0.3553305049    1.1072716438
C     1.2484603997    0.9956139492    1.1072716438
C     -0.6928432502    -1.4387038377    1.1072716438
C     1.5568046566    -0.3553305009    1.1072716438
C     0.692843254    -1.4387038358    1.1072716438
H     -0.0000000035    2.6761272138    1.1064843403
H     -2.0922805084    1.6685380238    1.1064843403
H     -2.6090311158    -0.5954943295    1.1064843403
H     2.0922805041    1.6685380293    1.1064843403
H     -1.1611280784    -2.4111073063    1.1064843403
H     2.6090311173    -0.5954943227    1.1064843403
H     1.1611280847    -2.4111073032    1.1064843403
Ar     0.    0.0000000007    -2.4994435877
```

ar2.inp – second Tr^+-Ar complex

```
! DLPNO-CCSD(T) aug-cc-pVQZ aug-cc-pVQZ/C TightSCF

%pal nproc 4 end
%maxcore 3000

*xyzfile 1 1 ar2.xyz
```

ar2.xyz

```
15

C    0.    1.5569338631    -0.9644859005
C    0.    0.6929011638    0.1189114816
C    0.    -0.6929011638    0.1189114816
C    0.    1.2485051025    -2.3154926056
C    0.    -1.5569338631    -0.9644859005
C    0.    0.    -2.9166804863
C    0.    -1.2485051025    -2.3154926056
H    0.    2.6091939306    -0.7243658859
H    0.    1.1592563656    1.0922220645
H    0.    -1.1592563656    1.0922220645
H    0.    2.0922502843    -2.9885507399
H    0.    -2.6091939306    -0.7243658859
H    0.    0.    -3.9959866446
H    0.    -2.0922502843    -2.9885507399
Ar    0.    0.    3.9113117926
```

ar3.inp – third Tr^+-Ar complex

```
! DLPNO-CCSD(T) aug-cc-pVQZ aug-cc-pVQZ/C TightSCF

%pal nproc 4 end
%maxcore 3000

*xyzfile 1 1 ar3.xyz
```

ar3.xyz

```
15

C     0.    1.5570302734    1.9056986357
C     0.    0.6928908461    2.9891226541
C     0.    -0.6928908461    2.9891226541
C     0.    1.2484438677    0.5547924677
C     0.    -1.5570302734    1.9056986357
C     0.    0.    -0.046634453
C     0.    -1.2484438677    0.5547924677
H     0.    2.6092525865    2.145996794
H     0.    1.1611008703    3.9615856661
H     0.    -1.1611008703    3.9615856661
H     0.    2.091957427    -0.1186275368
H     0.    -2.6092525865    2.145996794
H     0.    0.    -1.1258116159
H     0.    -2.091957427    -0.1186275368
Ar     0.    0.    -4.0019861334
```

Franck-Condon/Herzberg-Teller simulations in ORCA 4.1

`tr_guessorbs.inp` – guess orbitals for CASSCF

```
! RIJK Conv def2-SV(P) def2/JK XYZFile

%output
    Print[P_Basis] 2
    Print[P_MOs] 1
end

%maxcore 1500
%pal nproc 4 end

*xyz 1 1
  6     0.000000    1.609694    0.000000
  6     1.258509    1.003628    0.000000
  6     1.569336   -0.358191    0.000000
  6    -1.258509    1.003628    0.000000
  6     0.698420   -1.450284    0.000000
  6    -1.569336   -0.358191    0.000000
  6    -0.698420   -1.450284    0.000000
  1     0.000000    2.703505    0.000000
  1     2.113685    1.685608    0.000000
  1     2.635723   -0.601586    0.000000
  1    -2.113685    1.685608    0.000000
  1     1.173007   -2.435774    0.000000
  1    -2.635723   -0.601586    0.000000
  1    -1.173007   -2.435774    0.000000

*
```

`tr_cas-svp.inp` – initial active space setup

```
! RIJK Conv def2-SV(P) def2/JK MORead

%pal nproc 4 end
%maxcore 1500

%moinp "tr_guessorbs.gbw"

%casscf
    nel 6
    norb 7
    mult 1
    nroots 5
    trafostep ri
end

%scf
    Rotate {26, 31, 90} {27, 32, 90} end
end

*xyzfile 1 1 tr_guessorbs.xyz
```

`tr_cas-tzvp.inp` – projection to def2-TZVP basis set

```
! RIJK Conv def2-TZVP def2/JK MORead

%pal nproc 4 end
%maxcore 1500

%moinp "tr_cas-svp.gbw"

%casscf
    nel 6
    norb 7
    mult 1
    nroots 5
    trafostep ri
end

*xyzfile 1 1 tr_guessorbs.xyz
```

`tr_s0.inp` – optimization and frequencies for S_0

```
! def2-TZVP def2/JK MORead Opt NumFreq

%pal nproc 4 end
%maxcore 1500

%moinp "tr_cas-tzvp.gbw"

%casscf
    nel 6
    norb 7
    mult 1
    nroots 1
    trafostep ri
end

*xyzfile 1 1 tr_guessorbs.xyz
```

`tr_s1.inp` – optimization and frequencies for S_1

```
! def2-TZVP def2/JK MORead Opt NumFreq

%pal nproc 4 end
%maxcore 1500

%moinp "tr_cas-tzvp.gbw"

%casscf
    nel 6
    norb 7
    mult 1
    nroots 3
    weights[0] = 0, 1, 0
    trafostep ri
    switchconv 0.005
    switchstep nr
end

*xyzfile 1 1 tr_guessorbs.xyz
```

`tr_fcsim.inp` – convoluted Franck-Condon/Herzberg-Teller simulation

```
! def2-TZVP def2/JK MORead ESD(ABS)

%maxcore 1500
%pal nproc 4 end

%moinp "tr_s0.gbw"

%casscf
    nel 6
    norb 7
    mult 1
    nroots 3
    trafostep ri
    iroot 2
end

%esd
    gshessian "tr_s0.hess"
    eshessian "tr_s1.hess"
    doht true
    temp 0
    usej true
end

*xyzfile 1 1 tr_s0.xyz
```

`tr_fcsim-stick.inp` – stick Franck-Condon/Herzberg-Teller simulation

```
! def2-TZVP def2/JK MORead ESD(ABS)

%maxcore 2000
%pal nproc 6 end

%moinp "tr_s0.gbw"

%casscf
    nel 6
    norb 7
    mult 1
    nroots 3
    trafostep ri
    iroot 2
end

%esd
    gshessian "tr_s0.hess"
    eshessian "tr_s1.hess"
    doht true
    temp 0
    usej true
    lines gauss
    linew 10
    inlinew 5
end

*xyzfile 1 1 tr_s0.xyz
```

`tr_s1scan.inp` – Potential energy surface scan along $\nu 2$ and $\nu 7$ normal coordinates

```
! RIJK Conv def2-TZVP def2/JK MORead MTR

%pal nproc 4 end
%maxcore 1500

%moinp "tr_s0.gbw"

%mtr
    HessName "tr_s0.hess"
    ModeType normal
    MList 13, 18
    RSteps 60, 30
    LSteps 60, 30
    DDNC 0.1, 0.1
end

%casscf
    nel 6
    norb 7
    mult 1
    nroots 3
    trafostep ri
end

*xyzfile 1 1 tr_s0.xyz
```

`tr_s1scan.inp` – Potential energy surface scan along the two degenerate $\nu 7$ normal coordinates

```
! RIJK Conv def2-TZVP def2/JK MORead MTR

%pal nproc 4 end
%maxcore 10000

%moinp "tr_s0.gbw"

%mtr
    HessName "tr_s0.hess"
    ModeType normal
    MList 13, 18, 19
    RSteps 1, 30, 30
    LSteps 0, 30, 30
    DDNC 1.5, 0.1, 0.1
end

%casscf
    nel 6
    norb 7
    mult 1
    nroots 3
    trafostep ri
end

*xyzfile 1 1 tr_s0.xyz
```

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