HSO/HOS

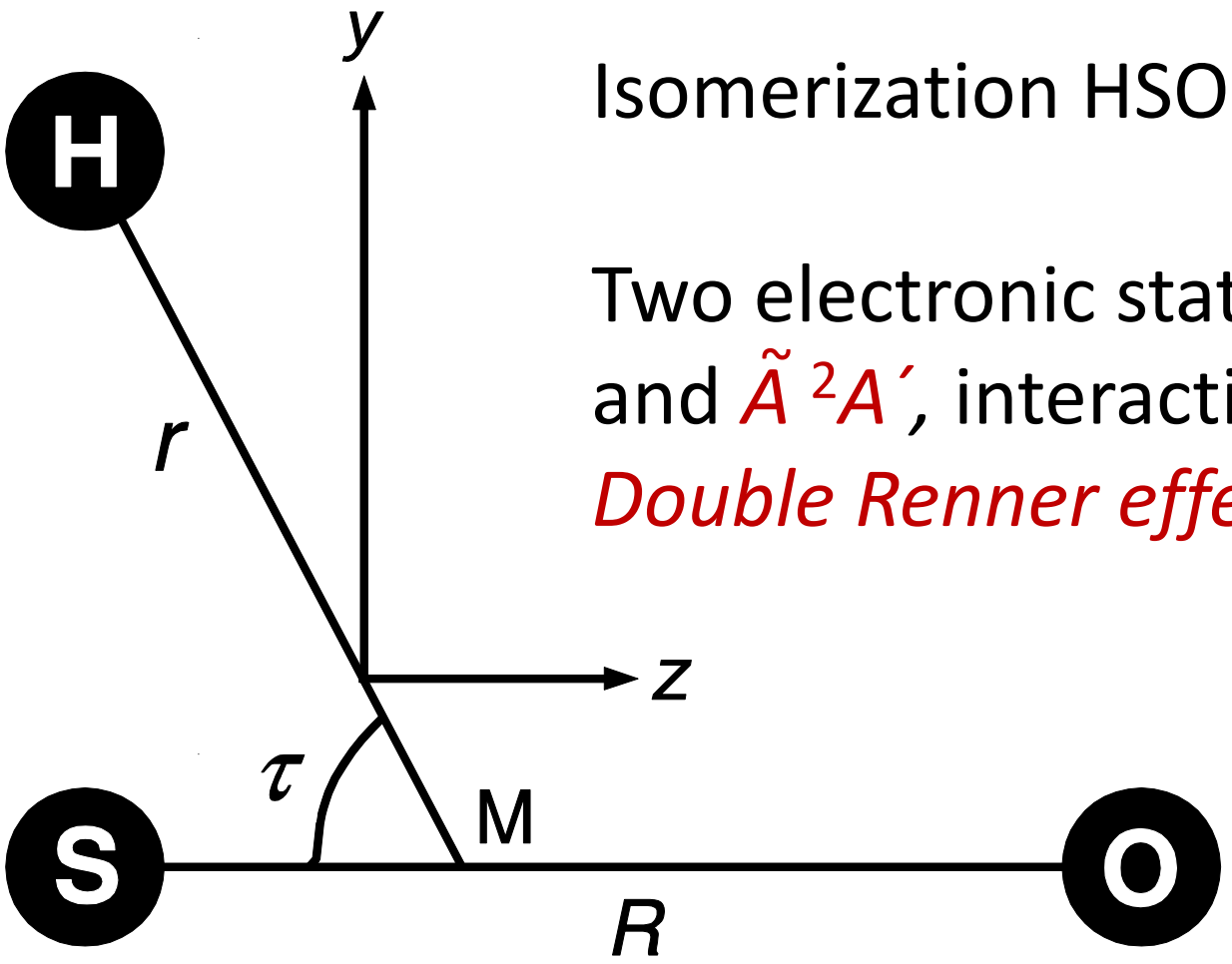
HSO is responsible for oxidation processes that produce atmospheric H_2SO_4.

HSO takes part in the ozone depletion cycle

Here: *ab initio* calculation of potential energy surfaces for $\tilde{X}\,^2A''$ and $\tilde{A}\,^2A'$ electronic states by the core-valence MR-SDCI+*Q*/[aug-cc-pCVQZ (S, O), aug-cc-pVQZ (H)] method (program MOLPRO); calculation of the rovibronic energies by means of the program DR.[a]

[a]Odaka, T. E.; Jensen, P.; Hirano, T. *J. Mol. Struct.* **2006**, *795*, 14-41.

HSO/HOS

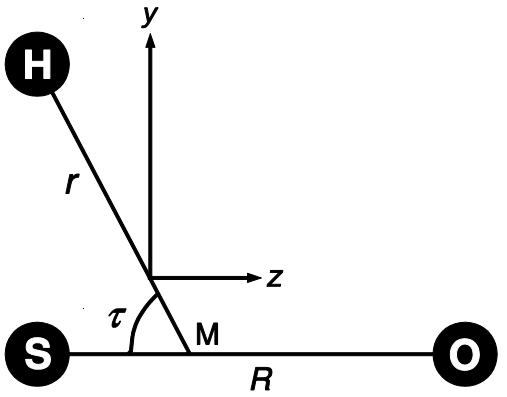


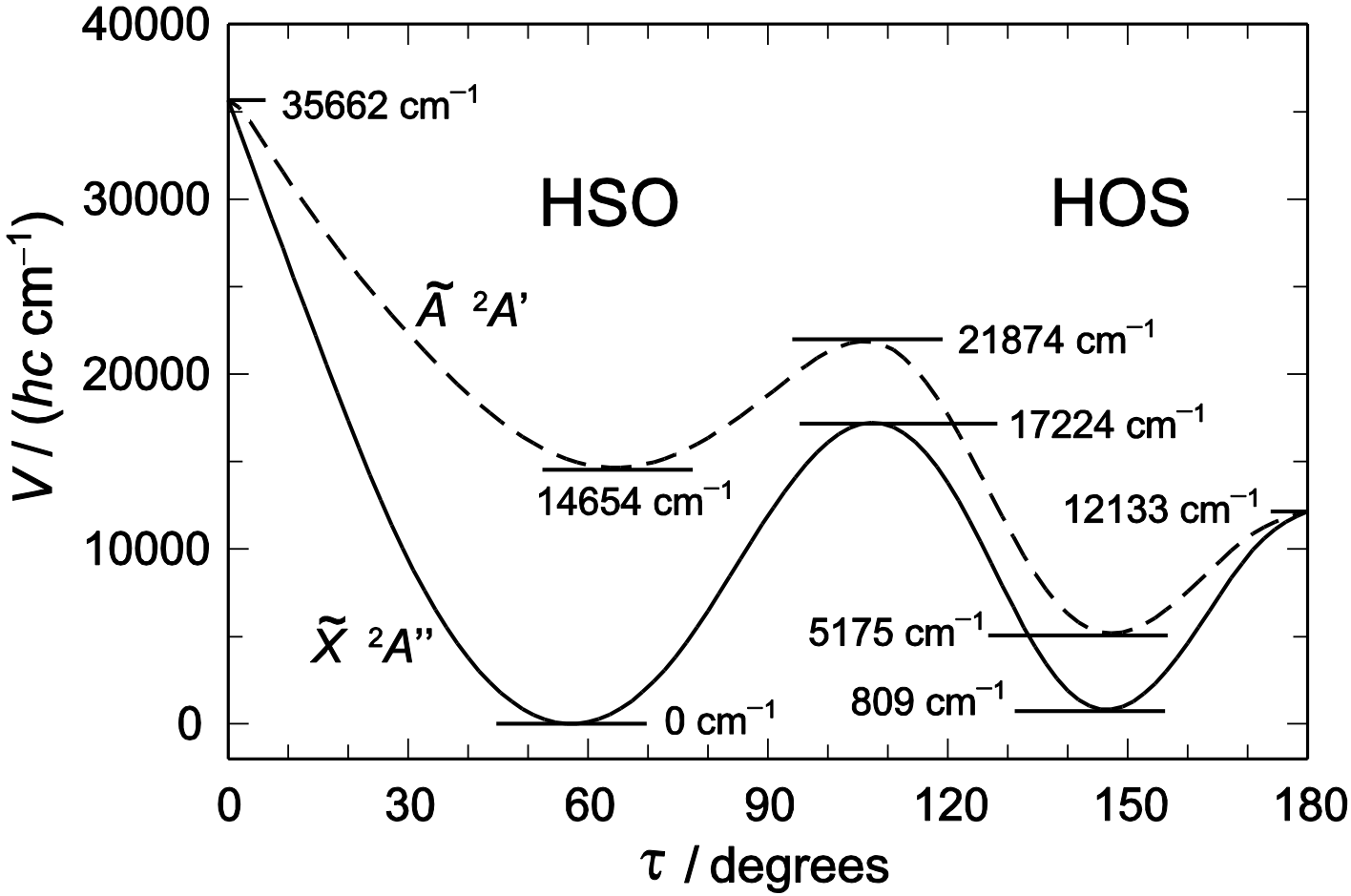
Isomerization HSO ↔ HOS

Two electronic states, $\tilde{X}\,^2A''$ and $\tilde{A}\,^2A'$, interacting by the *Double Renner effect*

HSO/HOS

Double Renner effect??

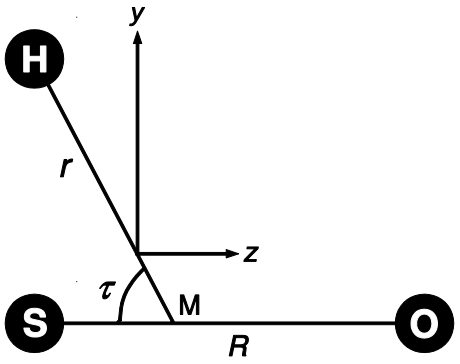




Minimum energy path for bending; distances „relax“ along the way

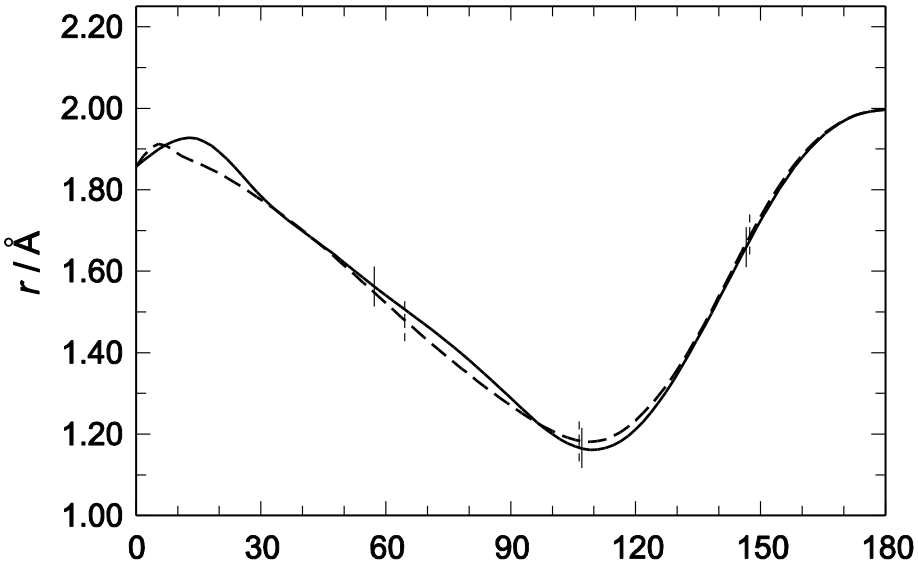
HSO/HOS

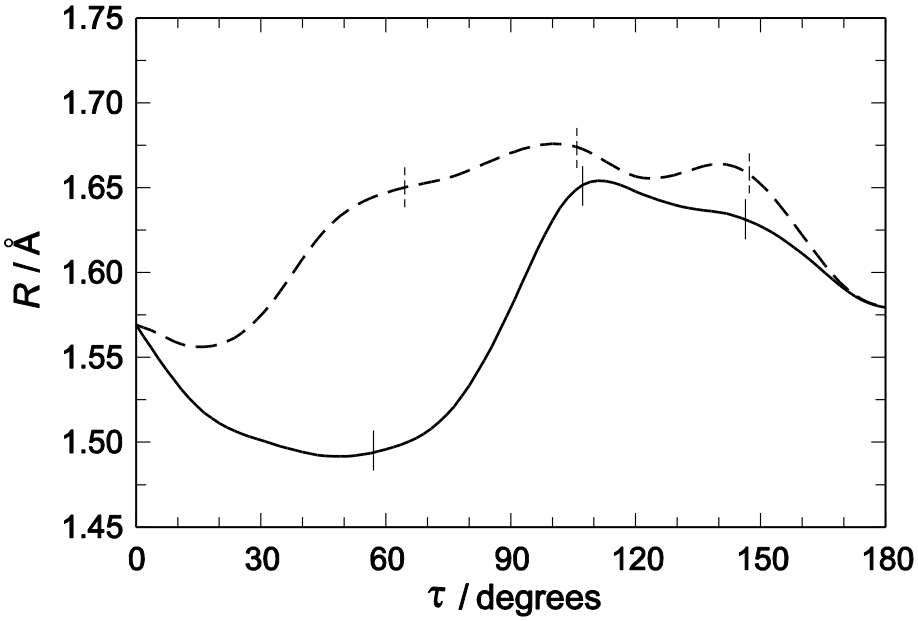
Minimum energy path for bending; distances „relax“ along the way



$\tilde{X}\,^2A''$: solid curves

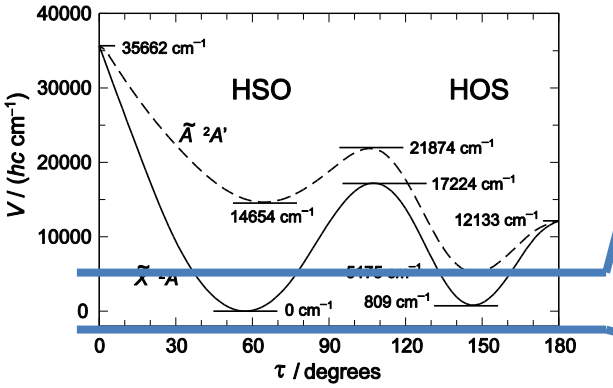
$\tilde{A}\,^2A'$: dashed curves

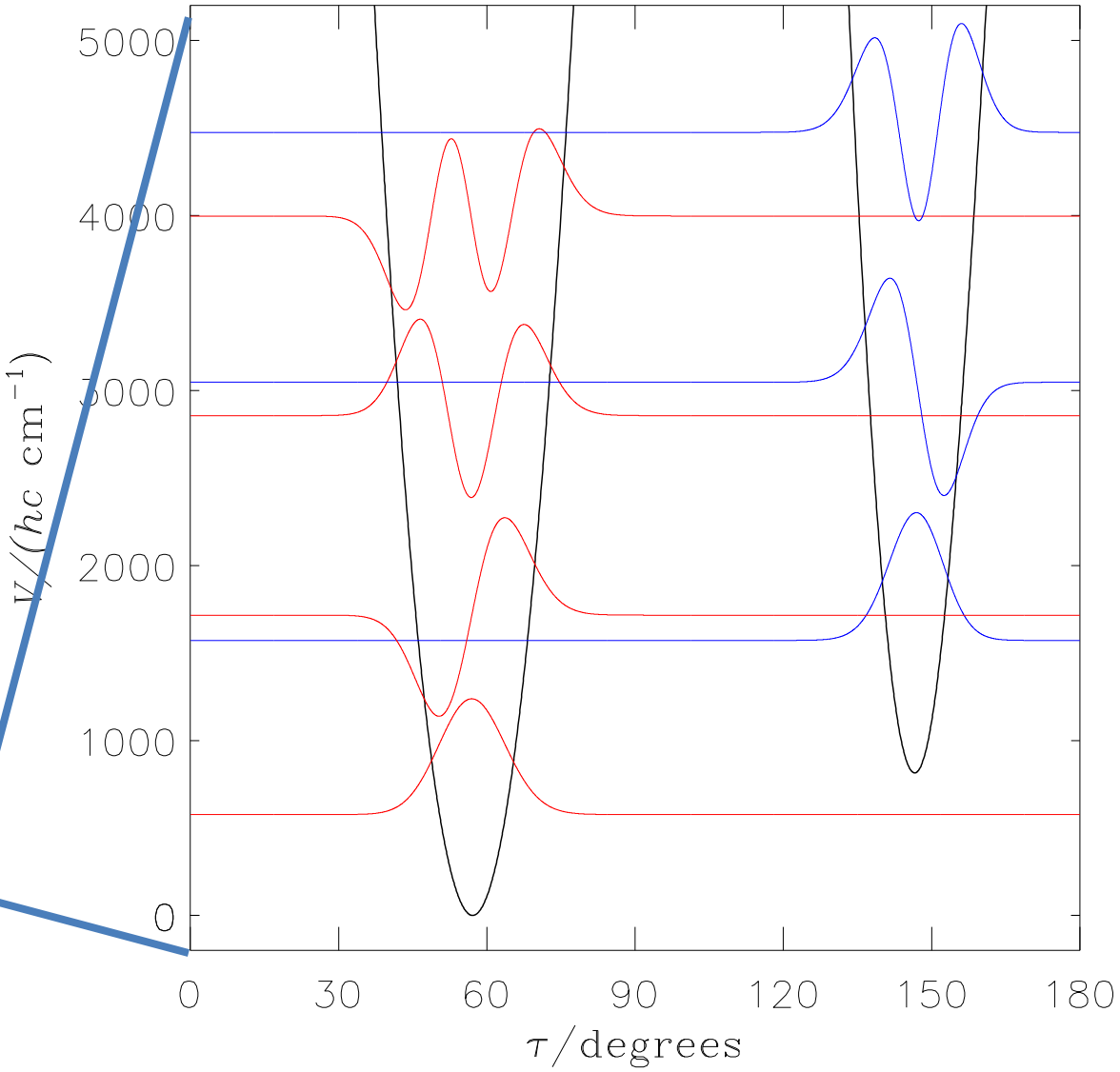




HSO/HOS

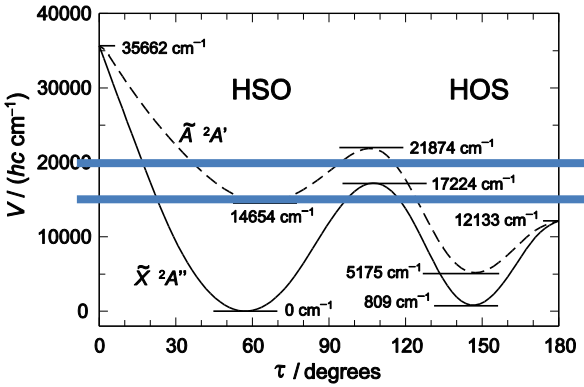
Bending-isomerization wavefunctions for the $\tilde{X}\,^2A''$ state





HSO/HOS

Bending-isomerization wavefunctions for the $\tilde{X}\,^2A''$ state



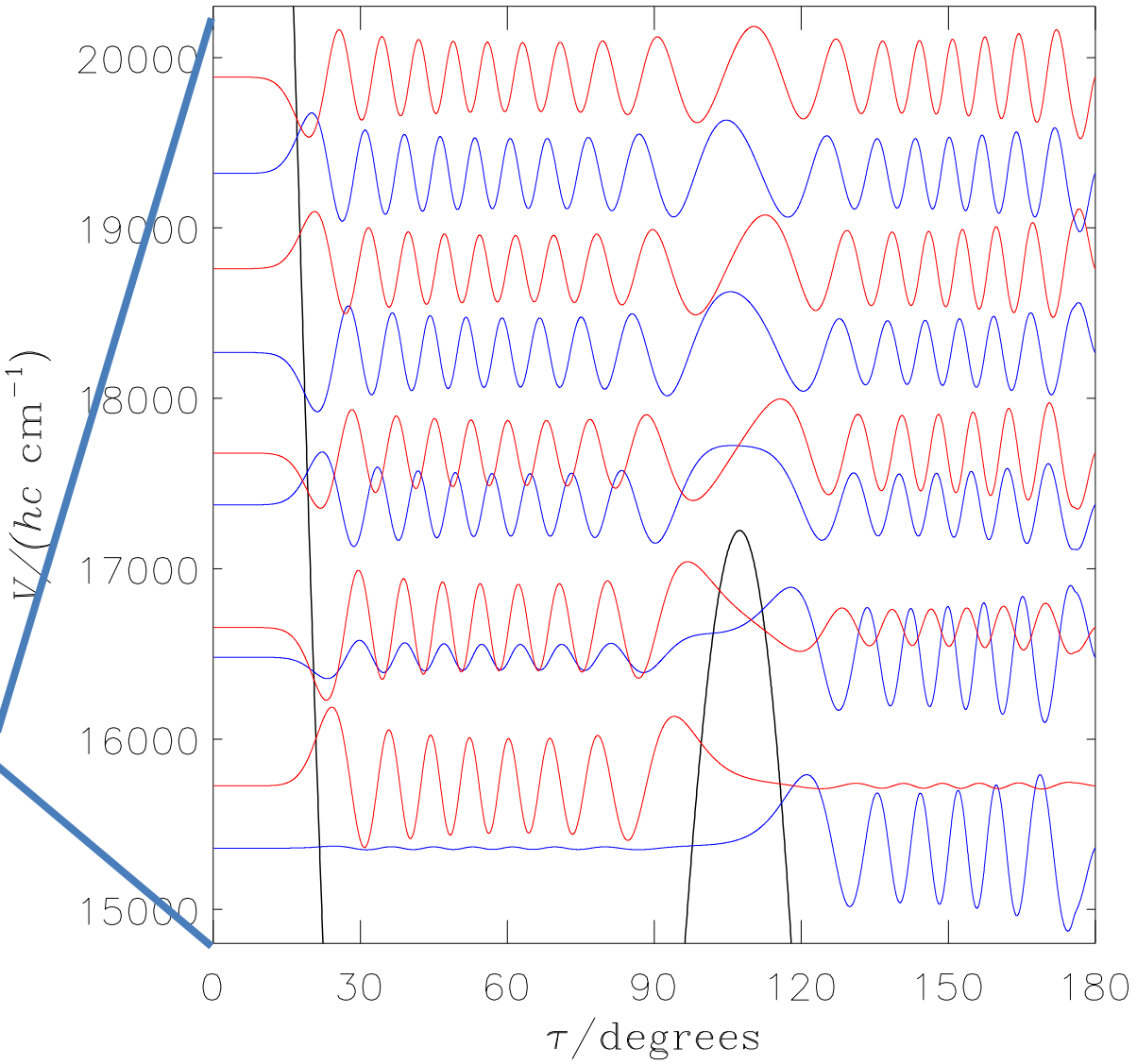


Table 3: Calculated fundamental term values of HSO/HOS (in cm^{-1})

State	Minimum		Present work	Exp[36,37]	CCSD(T)[27]
$\tilde{X}\ ^2A''$	HSO	ν_3	1024.85	1009.3551(10)[a,b]	1027
$\tilde{X}\ ^2A''$	HSO	ν_2	1087.79	1079(3)[c]	1102
$\tilde{X}\ ^2A''$	HSO	ν_1	2415.31	2325(3)[c]	2448
$\tilde{X}\ ^2A''$	HOS	ν_3	863.25		851
$\tilde{X}\ ^2A''$	HOS	ν_2	1189.90		1200
$\tilde{X}\ ^2A''$	HOS	ν_1	3652.12		3791
$\tilde{A}\ ^2A'$	HOS	ν_3	790.63		
$\tilde{A}\ ^2A'$	HOS	ν_2	1073.08		
$\tilde{A}\ ^2A'$	HOS	ν_1	3775.25		
$\tilde{A}\ ^2A'$	HSO	ν_3	745.27	703.497(19)[d]	
$\tilde{A}\ ^2A'$	HSO	ν_2	842.41	784.029(11)[d]	
$\tilde{A}\ ^2A'$	HSO	ν_1	2556.75		

[a] From Sears and McKellar.[36]

[b] Quantities in parentheses are quoted uncertainties in units of the last digit given.

[c] From Table 3 of Yoshikawa et al.[37]

[d] Calculated from the values of the parameters ω_2, ω_3, and x_{33} given in Table 6 of Yoshikawa et al.[37]

[27]Wang, N. X.; Wilson, A. K. *J. Phys. Chem. A* **2005**, *109*, 7187-7196

[36]Sears, T. J.; McKellar, A. R. W. *Mol. Phys.* **1983**, *49*, 25-32.

[37]Yoshikawa T.;Watanabe, A.; Sumiyoshi, Y.; Endo, Y. *J. Mol. Spectrosc.* **2009**, *254*, 119-125.

$$f_2(r,\tau) = \int_0^{\infty} \mathrm{d}R \int_0^{\pi} \sin\theta \, \mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi \int_0^{2\pi} \mathrm{d}\chi \int_{\mathrm{e,\,es}} \mathrm{d}V_{\mathrm{e}} \mathrm{d}V_{\mathrm{es}} \left| \Psi_{\mathrm{rve}}^{J, M_J, S, \Gamma_{\mathrm{rve}}, q} \right|^2 .$$

Example: Strong Renner effect/ SO coupling

HSO/HOS

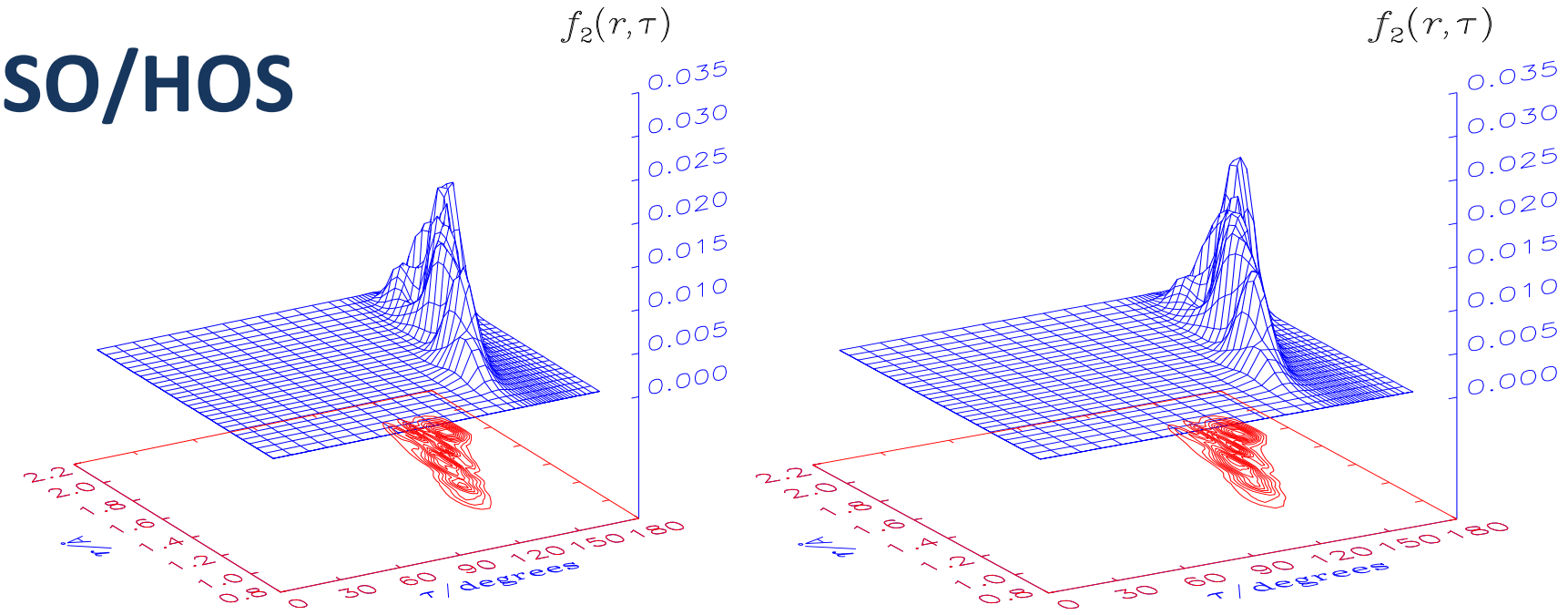


Figure 9: The function $f_2(r,\tau)$ (in units of Å^{-1}) for two $J = 1/2$ states with strong Renner interaction. Left panel: State with $N_{K_a K_c} = 1_{10}$, $\Gamma_{\mathrm{rve}} = A''$, and $E/hc = 12256.69\ \mathrm{cm}^{-1}$. Right panel: State with $N_{K_a K_c} = 0_{00}$, $\Gamma_{\mathrm{rve}} = A''$, and $E/hc = 12257.55\ \mathrm{cm}^{-1}$.

$$f_2(r,\tau) = \int_0^\infty \mathrm{d}R \int_0^\pi \sin\theta\,\mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi \int_0^{2\pi} \mathrm{d}\chi \int_{\mathrm{e,\,es}} \mathrm{d}V_\mathrm{e}\mathrm{d}V_\mathrm{es} \left|\Psi_\mathrm{rve}^{J,\,M_J,\,S,\,\Gamma_\mathrm{rve},\,q}\right|^2.$$

Example: Significant isomerization tunneling

HSO/HOS

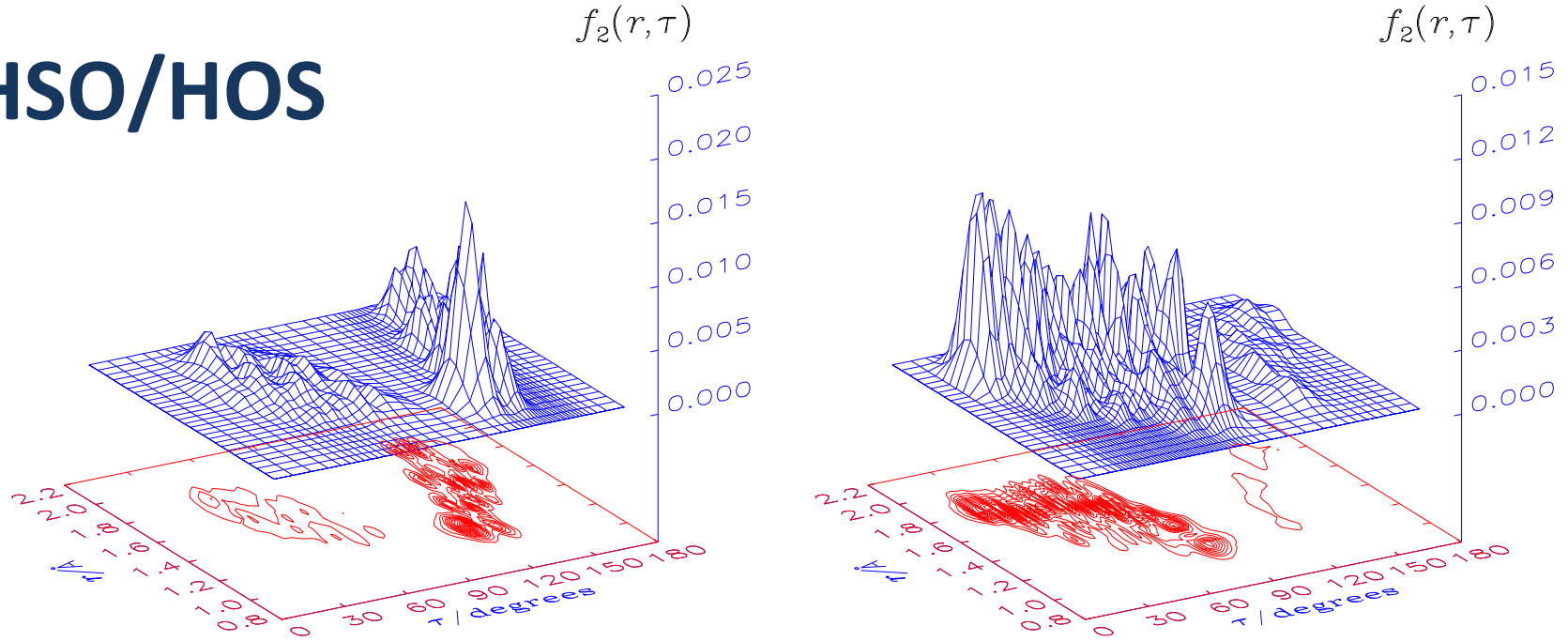
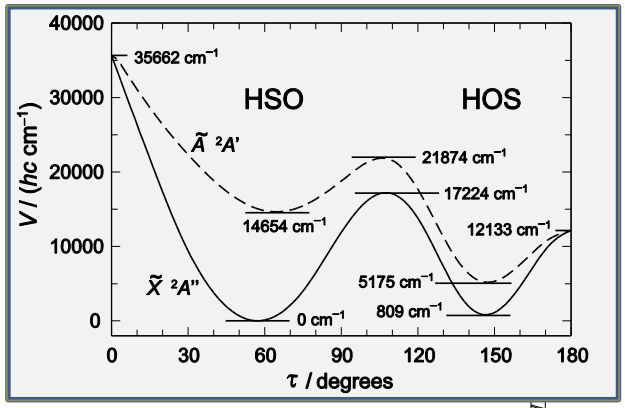


Figure 11: The functions $f_2(r,\tau)$ for two $J = 1/2$ states of HSO/HOS with significant HSO-HOS tunneling. Left panel: State with $N_{K_aK_c} = 1_{10}$, $\Gamma_\mathrm{rve} = A''$, and $E/hc = 15647.16\ \mathrm{cm}^{-1}$. Right panel: State with $N_{K_aK_c} = 1_{11}$, $\Gamma_\mathrm{rve} = A''$, and $E/hc = 15700.53\ \mathrm{cm}^{-1}$.

HSO/HOS



HSO geometry

$E \leq 14000$ cm^{-1}

14000 cm^{-1} < $E \leq$ 16000 cm^{-1}

16000 cm^{-1} < $E \leq$ 18000 cm^{-1}

18000 cm^{-1} < $E \leq$ 20000 cm^{-1}