

Electronic supplementary information to accompany:

**Symmetry matters: photodissociation dynamics of symmetrically
versus asymmetrically substituted phenols**

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Figure S1

H atom PHOFEX spectra for jet-cooled samples of (a) 3-FPhOH and (b) 4-MeOPhOH, with the respective S_1 - S_0 origins indicated.

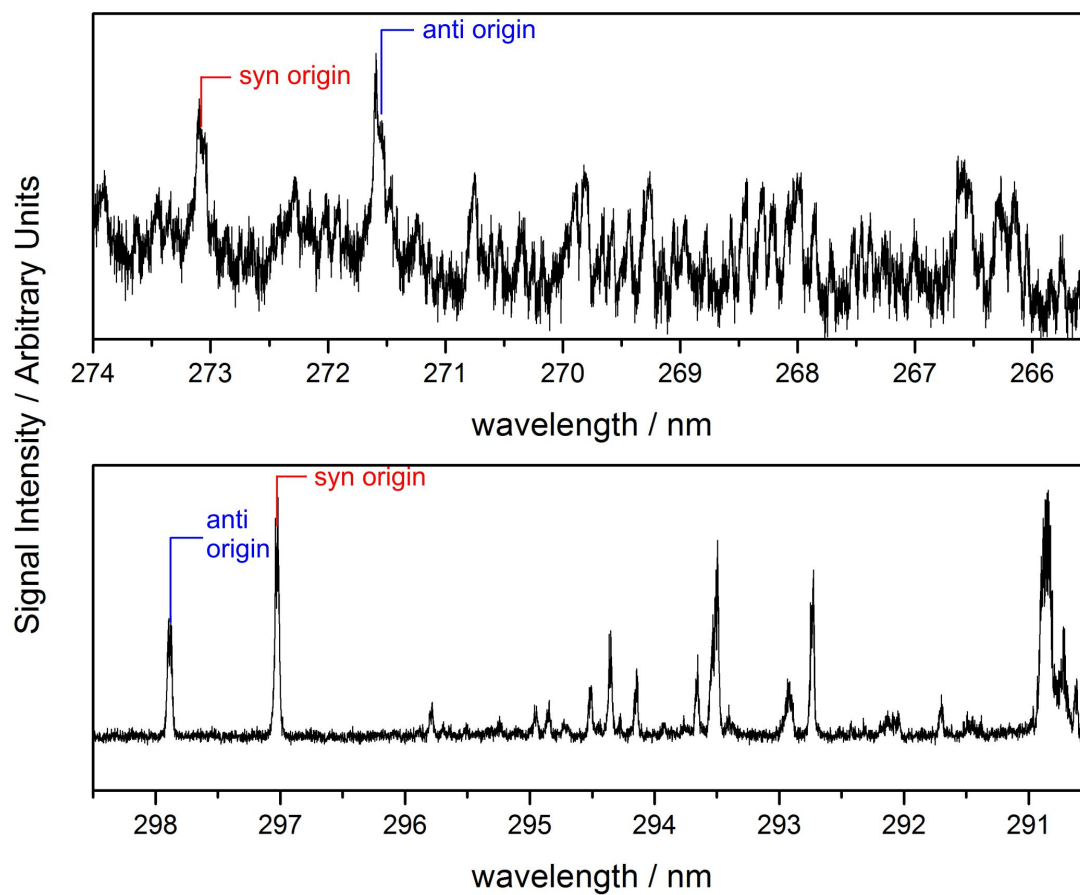


Table S1

Anharmonic wavenumbers (in cm^{-1}) of the normal modes of vibration of ground state 4-FPhO, 3-FPhO and 4-MeOPhO radicals calculated using DFT at the B3LYP/6-311+G(*d,p*) level and the Gaussian 03 computational suite. Normal modes are listed in Herzberg notation with the corresponding Wilson labels indicated (where appropriate) in parentheses.

Mode	4-FPhO		3-FPhO		4-MeOPhO	
	Wavenumber / cm^{-1}	Symmetry	Wavenumber / cm^{-1}	Symmetry	Wavenumber / cm^{-1}	Symmetry
1	3077	A'	3083	A'	3054	A'
2	3069	A'	3072	A'	3054	A'
3	3067	A'	3064	A'	3053	A'
4	3056	A'	3045	A'	3044	A'
5	1555	A'	1550	A'	3001	A'
6	1497	A'	1513	A'	2977	A'
7	1464	A'	1494	A'	1563	A'
8	1403 (ν_{7a})	A'	1453 (ν_{7a})	A'	1504	A'
9	1401	A'	1332	A'	1490	A'
10	1276	A'	1285	A'	1479 (ν_{7a})	A'
11	1239	A'	1228	A'	1471	A'
12	1230	A'	1159	A'	1431	A'
13	1128	A'	1130	A'	1396	A'
14	1086	A'	1062	A'	1285	A'
15	972	A'	981	A'	1264	A'
16	803	A'	904	A'	1230	A'
17	752	A'	722	A'	1178	A'
18	616	A'	523 (ν_{6a})	A'	1145	A'
19	458 (ν_{9b})	A'	499 (ν_{9b})	A'	1094	A'
20	453 (ν_{6a})	A'	485	A'	1012	A'
21	368 (ν_{18b})	A'	340 (ν_{18b})	A'	964	A'
22	973	A''	974	A''	803 (ν_1)	A'
23	963	A''	883	A''	738	A'
24	856	A''	860	A''	618	A'
25	777	A''	774	A''	519 (ν_{9b})	A'
26	735	A''	661	A''	446 (ν_{18b})	A'
27	506 (ν_{16b})	A''	578 (ν_{16b})	A''	393	A'
28	383 (ν_{16a})	A''	419 (ν_{16a})	A''	231	A'
29	322	A''	219	A''	2952	A''
30	130	A''	184	A''	1471	A''
31					1143	A''
32					965	A''
33					946	A''
34					845	A''
35					764	A''
36					742	A''
37					506	A''
38					384 (ν_{16a})	A''
39					329	A''
40					199	A''
41					137	A''
42					85	A''

Figure S2

Plot of TKER_{max} vs E_{phot} for 4-MeOPhOH, with the best-fit line of unit gradient superposed.

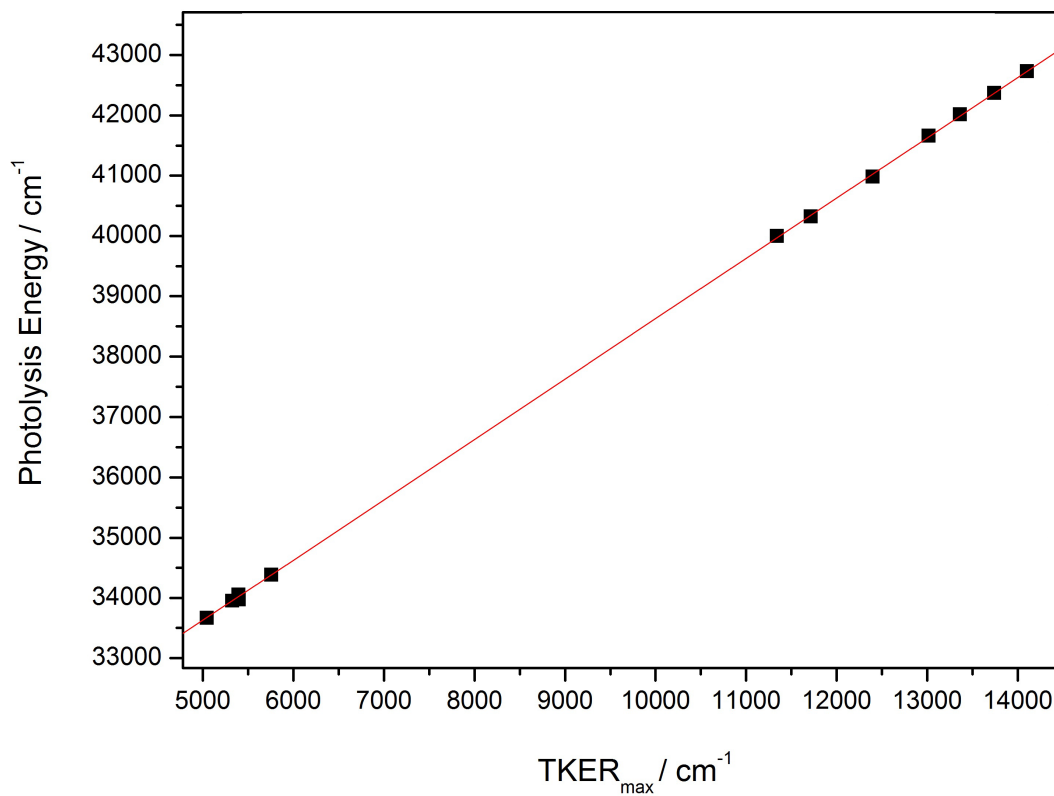


Figure S3

1-D PECs through the S_1 and S_2 PESs of 3-FPhOH calculated at the EOM-CCSD/cc-pVTZ level plotted as functions of $Q_x(a'')$, displayed in order of decreasing coupling strength, λ_x/ω_x .

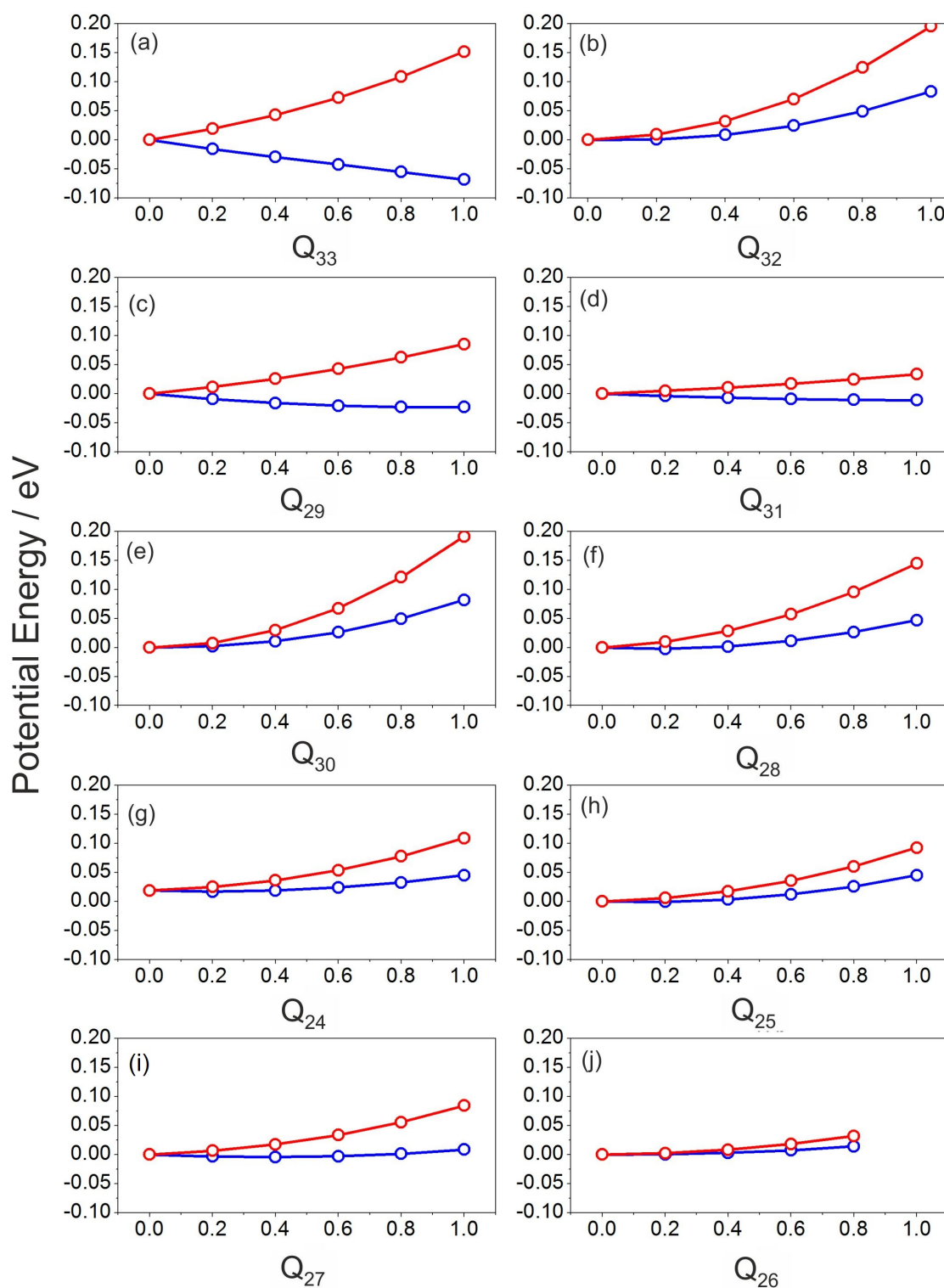


Figure S4

1-D PECs through the S_1 and S_2 PESs of 4-MeOPhOH calculated at the EOM-CCSD/cc-pVTZ level plotted as functions of $Q_x(a'')$, displayed in order of decreasing coupling strength, λ_x/ω_x .

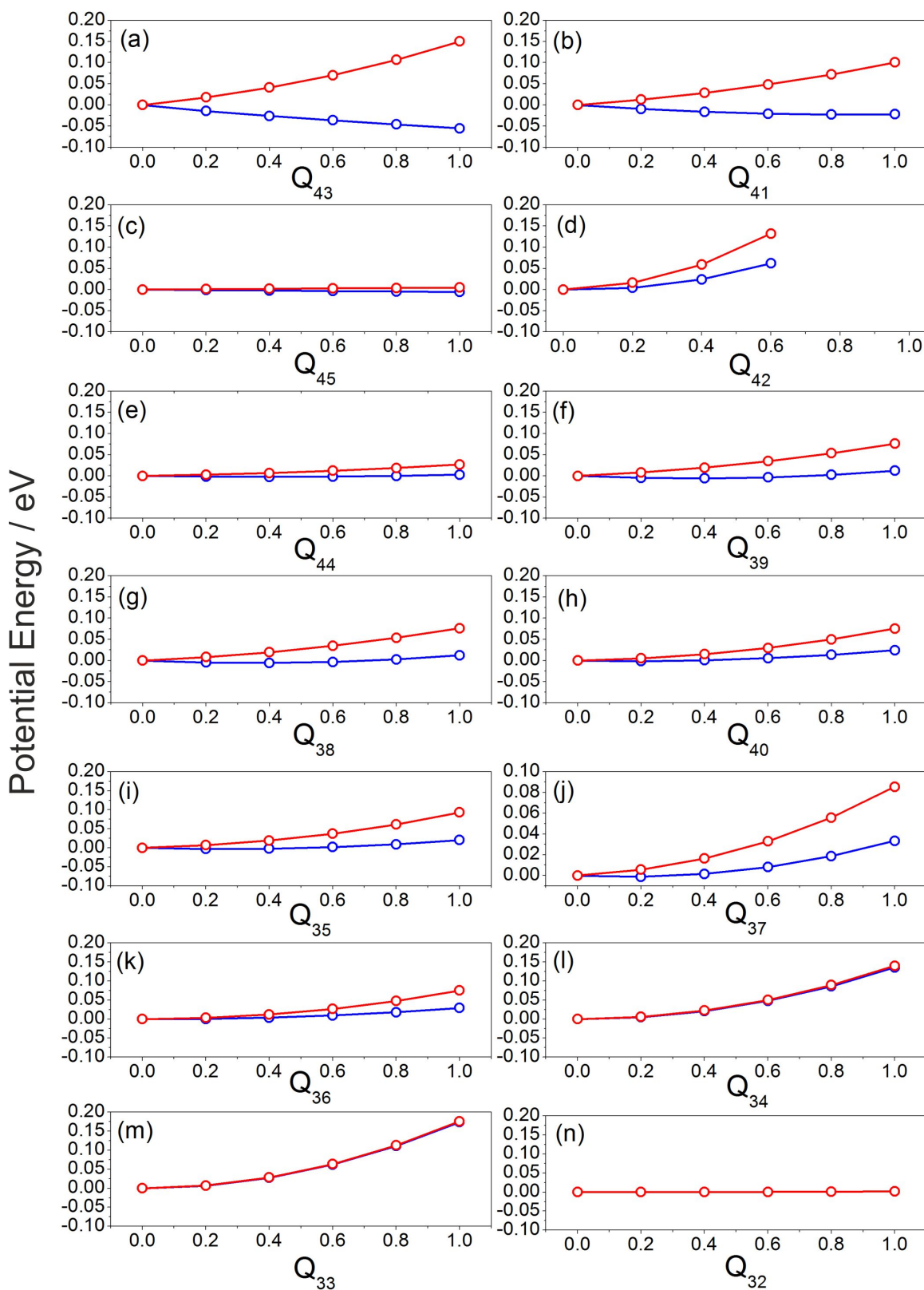


Figure S5

Nuclear motions associated with the dominant coupling motion at the $S_{1/2}$ S CI, *i.e.* with ν_{16a} in PhOH and 4-FPhOH, and with τ_{OH} in 3-FPhOH and 4-MeOPhOH.

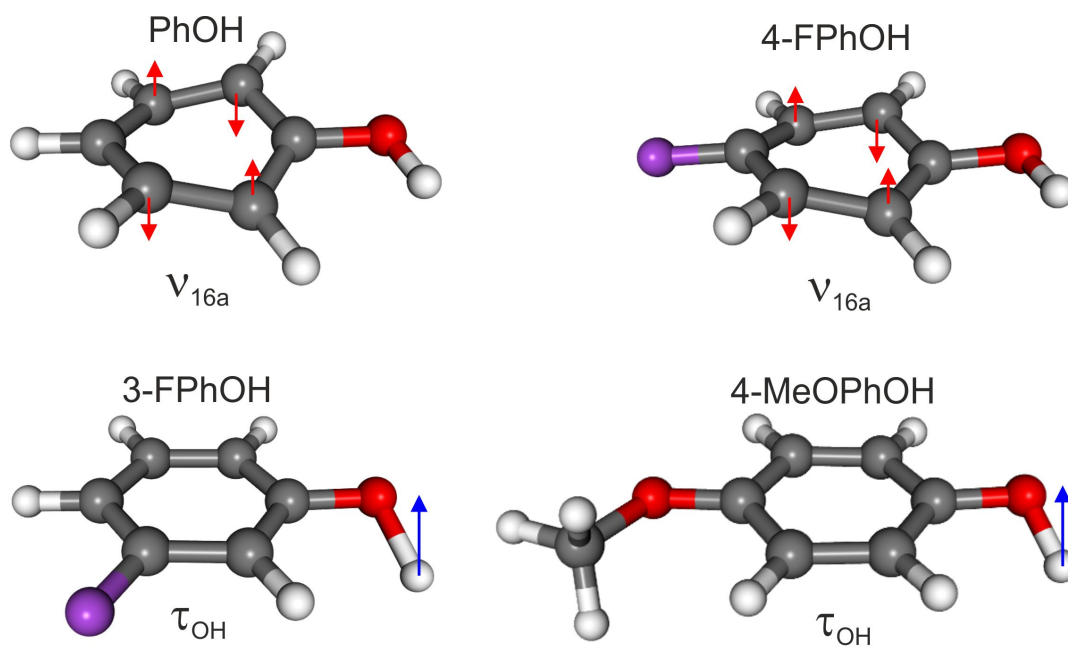


Figure S6

E_{int} spectra of the 4-MeOPhO(X) radicals formed by photolysis of jet-cooled 4-MeOPhOH molecules on selected resonances within the S_1 – S_0 band shown in fig. 2(b) of the main paper.

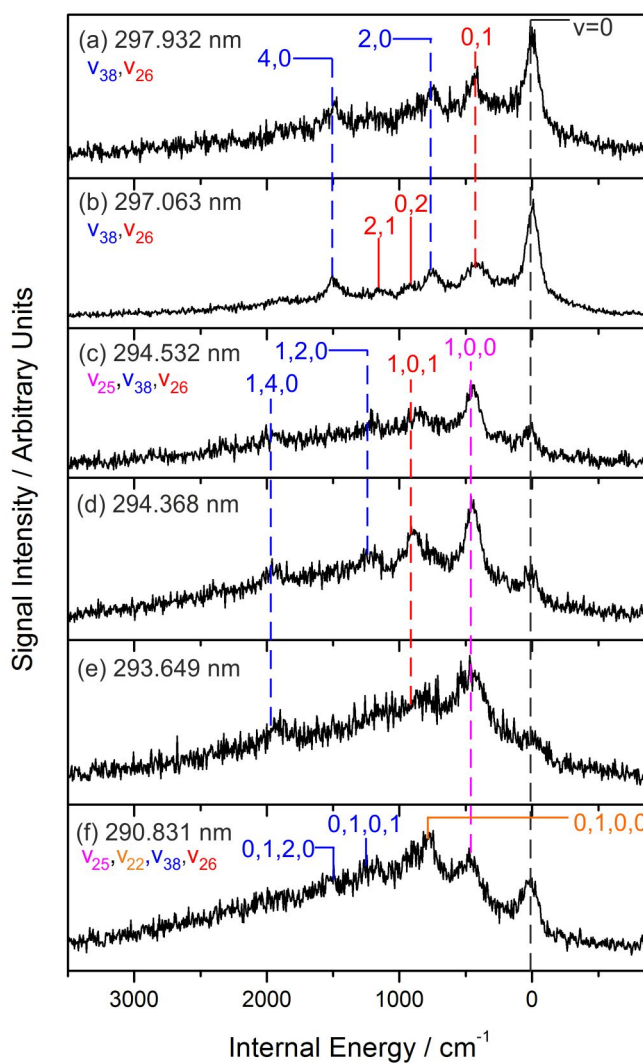


Figure S7

E_{int} spectra of the 4-MeOPhO(X) radicals formed by photolysis of jet-cooled 4-MeOPhOH molecules at various λ_{phot} corresponding to energies above the S_1/S_2 CI.

