Hybrid Quartic Force Fields with Atom-Specific Basis Sets: An Efficient Route to Calculate Anharmonic Vibrational Spectra

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Table S1: The dot products (Overlap) between the normal-mode vectors obtained from PESs generated with different electronic basis set pairs for acrylamide molecule using B3PW91 method.

Mode description	Basis set: def2-TZVPP	Overlap	Basis set: def2-SVP	Basis set: 6-311++G(2*df*,2*p*)	Overlap	Basis set: 6-31g(*d*)
NH_2 antisymmetric stretching	Mode 1	0.99	Mode 1	Mode 1	0.99	Mode 1
NH_2 symmetric stretching	Mode 2	0.99	Mode 2	Mode 2	0.99	Mode 2
CH_2 antisymmetric stretching	Mode 3	0.99	Mode 3	Mode 3	0.99	Mode 3
CH_2 symmetric stretching	Mode 5	0.99	Mode 5	Mode 5	0.93	Mode 5
NH_2 bending	Mode 8	0.99	Mode 8	Mode 8	0.99	Mode 8

Table S2 Harmonic (HO)**,** EHO, VSCF and VPT2 frequencies (cm^{-1}) for NH_2 antisymmetric stretching (for target site N7H9H10), calculated using def2-TZVPP (**H1**), def2-TZVP (**H2**), def2-SVP (**S1**), def2-SV (**S2**), and different combinations of ASHBS approach using two distinct layers of acrylamide (**M1**) molecule.

C1 (def2-TZVPP & def2-SV)												
	B3PW91				**B3LYP**				**MP2**			
	H1	**S2**	$L_1^a(M1)$	$L_2^a(M1)$	**H1**	**S2**	$L_1^a(M1)$	$L_2^a(M1)$	**H1**	**S2**	$L_1^a(M1)$	$L_2^a(M1)$
HO	3753.40	3685.16	3758.07	3754.55	3730.55	3663.89	3735.75	3731.67	3778.82	3706.82	3772.80	3776.28
VPT2	3553.73	3494.54	3546.58	3548.61	3526.80	3468.26	3514.14	3517.99	3657.03	3590.46	3632.11	3639.45
EHO	3562.90	3494.40	3566.10	3563.00	3539.40	3471.40	3543.00	3539.00	3586.00	3521.00	3582.30	3584.20
VSCF	3564.30	3495.60	3567.30	3564.40	3540.80	3472.40	3544.20	3540.30	3588.70	3523.50	3584.60	3586.90
C2 (def2-TZVP & def2-SV)												
	B3PW91				**B3LYP**				**MP2**			
	H2	**S2**	$L_1^a(M1)$	$L_2^a(M1)$	**H2**	**S2**	$L_1^a(M1)$	$L_2^a(M1)$	**H2**	**S2**	$L_1^a(M1)$	$L_2^a(M1)$
HO	3742.61	3685.16	3747.05	3743.18	3717.83	3663.89	3722.67	3718.27	3747.79	3706.82	3755.40	3748.10
VPT2	3546.03	3494.54	3550.50	3543.33	3519.54	3468.26	3522.06	3512.85	3659.58	3590.46	3673.63	3648.85
EHO	3554.10	3494.40	3557.10	3554.40	3529.70	3471.40	3531.80	3528.30	3563.80	3521.00	3571.80	3565.10
VSCF	3555.50	3495.60	3558.40	3555.80	3531.30	3472.40	3533.10	3529.80	3566.80	3523.50	3574.30	3568.00
C3 (def2-TZVPP & def2-SVP)												
	B3PW91				**B3LYP**				**MP2**			
	H1	**S1**	$L_1^a(M1)$	$L_2^a(M1)$	**H1**	**S1**	$L_1^a(M1)$	$L_2^a(M1)$	**H1**	**S1**	$L_1^a(M1)$	$L_2^a(M1)$
HO	3753.40	3752.89	3758.23	3754.70	3730.55	3726.00	3735.92	3731.83	3778.82	3803.02	3773.54	3777.27
VPT2	3553.73	3560.49	3547.54	3550.63	3526.80	3530.00	3514.79	3520.26	3657.03	3676.94	3633.34	3641.92
EHO	3562.90	3558.70	3566.90	3563.80	3539.40	3531.50	3543.90	3539.90	3586.00	3613.70	3582.80	3585.00
VSCF	3564.30	3559.80	3568.10	3565.20	3540.80	3532.40	3545.10	3541.30	3588.70	3615.80	3585.10	3587.60
C4 (def2-TZVP & def2-SVP)												
	B3PW91				**B3LYP**				**MP2**			
	H2	**S1**	$L_1^a(M1)$	$L_2^a(M1)$	**H2**	**S1**	$L_1^a(M1)$	$L_2^a(M1)$	**H2**	**S1**	$L_1^a(M1)$	$L_2^a(M1)$
HO	3742.61	3752.89	3747.15	3743.17	3717.83	3726.00	3722.77	3718.27	3747.79	3803.02	3756.35	3749.18
VPT2	3546.03	3560.49	3550.99	3544.67	3519.54	3530.00	3522.00	3513.41	3659.58	3676.94	3684.79	3659.30
EHO	3554.10	3558.70	3557.40	3554.70	3529.70	3531.50	3531.70	3528.30	3563.80	3613.70	3572.50	3566.10
VSCF	3555.50	3559.80	3558.70	3556.10	3531.30	3532.40	3532.90	3529.80	3566.80	3615.80	3575.00	3569.00

Table S3 Harmonic (HO), EHO, VSCF and VPT2 frequencies (cm^{-1}) for NH_2 symmetric stretching (for target site N7H9H10), calculated using def2-TZVPP (**H1**), def2-TZVP (**H2**), def2-SVP (**S1**), def2-SV (**S2**), and different combinations of ASHBS approach using two distinct layers of acrylamide (**M1**) molecule.

C1 (def2-TZVPP & def2-SV)												
	B3PW91				**B3LYP**				**MP2**			
	H1	**S2**	$L_1^a(M1)$	$L_2^a(M1)$	**H1**	**S2**	$L_1^a(M1)$	$L_2^a(M1)$	**H1**	**S2**	$L_1^a(M1)$	$L_2^a(M1)$
HO	3616.52	3564.67	3620.79	3617.50	3597.26	3546.41	3601.71	3598.17	3631.25	3578.69	3632.45	3630.53
VPT2	3443.21	3395.87	3438.56	3439.28	3421.03	3373.74	3412.12	3414.32	3511.17	3467.93	3499.08	3499.90
EHO	3434.50	3378.10	3438.60	3434.50	3414.20	3358.40	3418.60	3413.80	3443.20	3391.40	3444.90	3442.30
VSCF	3465.00	3409.50	3469.00	3465.10	3444.90	3390.10	3449.30	3444.50	3474.60	3423.10	3476.40	3473.90
C2 (def2-TZVP & def2-SV)												
	B3PW91				**B3LYP**				**MP2**			
	H2	**S2**	$L_1^a(M1)$	$L_2^a(M1)$	**H2**	**S2**	$L_1^a(M1)$	$L_2^a(M1)$	**H2**	**S2**	$L_1^a(M1)$	$L_2^a(M1)$
HO	3607.87	3564.67	3612.81	3608.72	3586.81	3546.41	3592.04	3587.57	3600.89	3578.69	3611.88	3602.50
VPT2	3436.06	3395.87	3440.05	3434.08	3414.75	3373.74	3416.11	3408.63	3507.74	3467.93	3525.04	3501.97
EHO	3426.50	3378.10	3430.70	3426.60	3405.70	3358.40	3408.80	3404.10	3419.90	3391.40	3432.30	3422.00
VSCF	3457.00	3409.50	3461.20	3457.10	3436.50	3390.10	3439.60	3434.90	3450.80	3423.10s	3462.90	3452.80
C3 (def2-TZVPP & def2-SVP)												
	B3PW91				**B3LYP**				**MP2**			
	H1	**S1**	$L_1^a(M1)$	$L_2^a(M1)$	**H1**	**S1**	$L_1^a(M1)$	$L_2^a(M1)$	**H1**	**S1**	$L_1^a(M1)$	$L_2^a(M1)$
HO	3616.52	3611.55	3620.78	3617.46	3597.26	3588.56	3601.70	3598.13	3631.25	3653.24	3632.78	3630.98
VPT2	3443.21	3442.90	3439.73	3441.00	3421.03	3417.31	3413.23	3416.33	3511.17	3533.46	3499.74	3501.41
EHO	3434.50	3427.90	3439.30	3435.30	3414.20	3405.00	3419.50	3414.60	3443.20	3470.20	3445.10	3442.90
VSCF	3465.00	3458.70	3469.80	3465.80	3444.90	3435.90	3450.10	3445.40	3474.60	3501.10	3476.60	3474.30
C4 (def2-TZVP & def2-SVP)												
	B3PW91				**B3LYP**				**MP2**			
	H2	**S1**	$L_1^a(M1)$	$L_2^a(M1)$	**H2**	**S1**	$L_1^a(M1)$	$L_2^a(M1)$	**H2**	**S1**	$L_1^a(M1)$	$L_2^a(M1)$
HO	3607.87	3611.55	3612.81	3608.62	3586.81	3588.56	3592.04	3587.47	3600.89	3653.24	3612.37	3603.13
VPT2	3436.06	3442.90	3440.54	3435.33	3414.75	3417.31	3415.88	3408.91	3507.74	3533.46	3532.93	3509.42
EHO	3426.50	3427.90	3431.10	3426.90	3405.70	3405.00	3408.70	3403.90	3419.90	3470.20	3432.80	3422.70
VSCF	3457.00	3458.70	3461.60	3457.50	3436.50	3435.90	3439.40	3434.80	3450.80	3501.10	3463.40	3453.50

Table S4 Harmonic (HO), EHO, VSCF and VPT2 frequencies (cm^{-1}) for NH_2 bending (for target site N7H9H10), calculated using def2-TZVPP (**H1**), def2-TZVP (**H2**), def2-SVP (**S1**), def2-SV (**S2**), and different combinations of ASHBS approach using two distinct layers of acrylamide (M1) molecule.

C1 (def2-TZVPP & def2-SV)												
	B3PW91				**B3LYP**				**MP2**			
	H1	**S2**	$L_1^a(M1)$	$L_2^a(M1)$	**H1**	**S2**	$L_1^a(M1)$	$L_2^a(M1)$	**H1**	**S2**	$L_1^a(M1)$	$L_2^a(M1)$
HO	1614.12	1619.68	1609.49	1612.59	1619.00	1616.95	1612.48	1616.95	1621.73	1647.03	1623.06	1621.15
VPT2	1575.92	1583.59	1577.98	1577.07	1579.93	1580.57	1583.16	1581.02	1574.00	1594.61	1576.40	1577.60
EHO	1589.20	1596.00	1586.70	1589.40	1593.10	1592.40	1589.00	1593.00	1596.20	1622.10	1597.30	1595.90
VSCF	1589.50	1596.20	1587.00	1589.80	1593.30	1592.50	1589.40	1593.20	1596.50	1622.20	1597.70	1596.30
C2 (def2-TZVP & def2-SV)												
	B3PW91				**B3LYP**				**MP2**			
	H2	**S2**	$L_1^a(M1)$	$L_2^a(M1)$	**H2**	**S2**	$L_1^a(M1)$	$L_2^a(M1)$	**H2**	**S2**	$L_1^a(M1)$	$L_2^a(M1)$
HO	1616.24	1619.68	1617.65	1617.09	1621.22	1616.95	1622.28	1621.93	1624.15	1647.03	1636.17	1627.31
VPT2	1575.83	1583.59	1577.02	1577.58	1577.85	1580.57	1580.72	1582.39	1569.03	1594.61	1589.89	1579.25
EHO	1590.30	1596.00	1591.70	1591.80	1592.00	1592.40	1594.30	1595.50	1595.80	1622.10	1606.60	1598.60
VSCF	1590.60	1596.20	1592.10	1592.10	1592.30	1592.50	1594.70	1595.80	1596.10	1622.20	1606.90	1598.90
C3 (def2-TZVPP & def2-SVP)												
	B3PW91				**B3LYP**				**MP2**			
	H1	**S1**	$L_1^a(M1)$	$L_2^a(M1)$	**H1**	**S1**	$L_1^a(M1)$	$L_2^a(M1)$	**H1**	**S1**	$L_1^a(M1)$	$L_2^a(M1)$
HO	1614.12	1588.46	1608.86	1611.54	1619.00	1587.07	1611.80	1615.81	1621.73	1621.80	1622.10	1619.48
VPT2	1575.92	1557.18	1577.40	1575.35	1579.93	1548.44	1583.03	1580.13	1574.00	1577.73	1574.95	1574.36
EHO	1589.20	1569.30	1585.90	1588.30	1593.10	1566.60	1588.30	1591.40	1596.20	1598.80	1596.70	1595.20
VSCF	1589.50	1569.60	1586.40	1588.60	1593.30	1566.80	1588.70	1591.80	1596.50	1598.90	1597.10	1595.50
C4 (def2-TZVP & def2-SVP)												
	B3PW91				**B3LYP**				**MP2**			
	H2	**S1**	$L_1^a(M1)$	$L_2^a(M1)$	**H2**	**S1**	$L_1^a(M1)$	$L_2^a(M1)$	**H2**	**S1**	$L_1^a(M1)$	$L_2^a(M1)$
HO	1616.24	1588.46	1617.26	1616.72	1621.22	1587.07	1621.82	1621.54	1624.15	1621.80	1635.39	1626.69
VPT2	1575.83	1557.18	1575.16	1574.92	1577.85	1548.44	1579.71	1580.93	1569.03	1577.73	1588.14	1576.77
EHO	1590.30	1569.30	1590.70	1590.00	1592.00	1566.60	1593.90	1595.00	1595.80	1598.80	1605.60	1597.60
VSCF	1590.60	1569.60	1591.10	1590.30	1592.30	1566.80	1594.30	1595.40	1596.10	1598.90	1605.90	1597.90

Table S5 Harmonic (HO), EHO, VSCF and VPT2 frequencies (cm^{-1}) for CH_2 antisymmetric stretching (for target site C1H2H3), calculated using def2-TZVPP (**H1**), def2-TZVP (**H2**), def2-SVP (**S1**), def2-SV (**S2**), and different combinations of ASHBS approach using two distinct layers of acrylamide (**M1**) molecule.

C1 (def2-TZVPP & def2-SV)												
	B3PW91				**B3LYP**				**MP2**			
	H1	**S2**	$L_1^b(M1)$	$L_2^b(M1)$	**H1**	**S2**	$L_1^b(M1)$	$L_2^b(M1)$	**H1**	**S2**	$L_1^b(M1)$	$L_2^b(M1)$
HO	3249.15	3248.02	3248.18	3248.59	3240.38	3233.94	3238.78	3239.69	3298.51	3283.59	3306.47	3300.22
VPT2	3109.87	3107.51	3109.90	3108.33	3103.89	3094.59	3100.44	3103.94	3158.15	3141.46	3170.30	3158.75
EHO	3077.90	3073.60	3077.00	3076.80	3067.90	3058.00	3066.60	3066.70	3127.00	3109.80	3131.50	3128.50
VSCF	3078.20	3073.70	3077.90	3077.40	3067.90	3057.90	3067.10	3067.00	3127.70	3109.70	3132.50	3129.40
C2 (def2-TZVP & def2-SV)												
	B3PW91				**B3LYP**				**MP2**			
	H2	**S2**	$L_1^b(M1)$	$L_2^b(M1)$	**H2**	**S2**	$L_1^b(M1)$	$L_2^b(M1)$	**H2**	**S2**	$L_1^b(M1)$	$L_2^b(M1)$
HO	3248.48	3248.02	3246.87	3248.42	3239.39	3233.94	3236.87	3239.17	3287.82	3283.59	3287.68	3288.05
VPT2	3110.87	3107.51	3107.40	3109.20	3104.24	3094.59	3100.31	3107.26	3146.41	3141.46	3147.68	3148.93
EHO	3077.00	3073.60	3075.50	3076.60	3066.80	3058.00	3064.70	3066.30	3115.50	3109.80	3116.10	3116.40
VSCF	3077.30	3073.70	3076.30	3077.20	3066.90	3057.90	3065.10	3066.50	3116.20	3109.70	3116.60	3117.10
C3 (def2-TZVPP & def2-SVP)												
	B3PW91				**B3LYP**				**MP2**			
	H1	**S1**	$L_1^b(M1)$	$L_2^b(M1)$	**H1**	**S1**	$L_1^b(M1)$	$L_2^b(M1)$	**H1**	**S1**	$L_1^b(M1)$	$L_2^b(M1)$
HO	3249.15	3267.21	3247.69	3248.40	3240.38	3250.41	3238.34	3239.53	3298.51	3332.86	3307.08	3300.04
VPT2	3109.87	3121.98	3109.18	3108.29	3103.89	3103.65	3099.14	3103.90	3158.15	3187.64	3163.94	3158.70
EHO	3077.90	3090.50	3077.00	3076.80	3067.90	3072.40	3066.20	3066.80	3127.00	3156.20	3132.80	3128.20
VSCF	3078.20	3091.00	3078.30	3077.30	3067.90	3072.50	3066.70	3067.00	3127.70	3156.40	3134.40	3129.10
C4 (def2-TZVP & def2-SVP)												
	B3PW91				**B3LYP**				**MP2**			
	H2	**S1**	$L_1^b(M1)$	$L_2^b(M1)$	**H2**	**S1**	$L_1^b(M1)$	$L_2^b(M1)$	**H2**	**S1**	$L_1^b(M1)$	$L_2^b(M1)$
HO	3248.48	3267.21	3246.58	3248.31	3239.39	3250.41	3236.64	3239.09	3287.82	3332.86	3289.08	3288.01
VPT2	3110.87	3121.98	3108.65	3109.38	3104.24	3103.65	3097.70	3107.44	3146.41	3187.64	3149.35	3147.78
EHO	3077.00	3090.50	3075.70	3076.60	3066.80	3072.40	3064.20	3066.20	3115.50	3156.20	3118.60	3116.10
VSCF	3077.30	3091.00	3076.80	3077.20	3066.90	3072.50	3064.80	3066.50	3116.20	3156.40	3119.70	3116.90

Table S6 Harmonic (HO), EHO, VSCF and VPT2 frequencies (cm^{-1}) for CH_2 symmetric stretching (for target site C1H2H3), calculated using def2-TZVPP (**H1**), def2-TZVP (**H2**), def2-SVP (**S1**), def2-SV (**S2**), and different combinations of ASHBS approach using two distinct layers of acrylamide (**M1**) molecule.

C1 (def2-TZVPP & def2-SV)												
	B3PW91				**B3LYP**				**MP2**			
	H1	**S2**	$L_1^b(M1)$	$L_2^b(M1)$	**H1**	**S2**	$L_1^b(M1)$	$L_2^b(M1)$	**H1**	**S2**	$L_1^b(M1)$	$L_2^b(M1)$
HO	3148.52	3147.65	3148.98	3147.28	3143.38	3137.53	3142.35	3141.57	3190.23	3178.62	3193.56	3191.13
VPT2	2988.83	2983.27	2994.09	2991.40	2973.31	2972.01	2973.56	2971.34	3092.49	3009.63	3010.79	3026.36
EHO	3017.30	3001.90	3015.80	3015.80	3005.20	2979.50	2990.70	3001.70	3047.80	3042.00	3018.10	3049.90
VSCF	3019.30	3003.00	3019.00	3018.30	3005.40	2984.10	2993.60	3002.20	3063.00	3046.10	3032.00	3064.10
C2 (def2-TZVP & def2-SV)												
	B3PW91				**B3LYP**				**MP2**			
	H2	**S2**	$L_1^b(M1)$	$L_2^b(M1)$	**H2**	**S2**	$L_1^b(M1)$	$L_2^b(M1)$	**H2**	**S2**	$L_1^b(M1)$	$L_2^b(M1)$
HO	3149.08	3147.65	3148.68	3147.94	3143.61	3137.53	3141.97	3141.50	3179.63	3178.62	3182.30	3179.64
VPT2	2987.36	2983.27	2985.33	2987.51	2972.31	2972.01	2973.18	2965.60	3013.14	3009.63	3028.01	3015.77
EHO	3016.40	3001.90	3015.50	3014.20	3001.90	2979.50	2995.50	2990.20	3036.40	3042.00	3045.30	3043.00
VSCF	3017.80	3003.00	3019.30	3014.90	3002.70	2984.10	2996.80	2993.90	3052.00	3046.10	3054.90	3052.60
C3 (def2-TZVPP & def2-SVP)												
Algorithm	**B3PW91**				**B3LYP**				**MP2**			
	H1	**S1**	$L_1^b(M1)$	$L_2^b(M1)$	**H1**	**S1**	$L_1^b(M1)$	$L_2^b(M1)$	**H1**	**S1**	$L_1^b(M1)$	$L_2^b(M1)$
HO	3148.52	3152.78	3150.02	3147.06	3143.38	3140.42	3144.02	3141.44	3190.23	3210.03	3201.66	3191.21
VPT2	2988.83	2998.04	3000.23	2989.63	2973.31	2979.67	2981.01	2970.66	3092.49	3049.11	3041.16	3025.61
EHO	3017.30	3018.60	3010.40	3015.50	3005.20	3005.40	3009.00	3001.60	3047.80	3070.20	3051.90	3048.40
VSCF	3019.30	3024.20	3024.70	3017.90	3005.40	3008.00	3010.20	3002.10	3063.00	3081.90	3071.70	3063.70
C4 (def2-TZVP & def2-SVP)												
	B3PW91				**B3LYP**				**MP2**			
	H2	**S1**	$L_1^b(M1)$	$L_2^b(M1)$	**H2**	**S1**	$L_1^b(M1)$	$L_2^b(M1)$	**H2**	**S1**	$L_1^b(M1)$	$L_2^b(M1)$
HO	3149.08	3152.78	3149.88	3147.60	3143.61	3140.42	3143.77	3141.21	3179.63	3210.03	3184.67	3179.83
VPT2	2987.36	2998.04	3000.81	2984.84	2972.31	2979.67	2986.01	2964.36	3013.14	3049.11	3032.38	3018.02
EHO	3016.40	3018.60	3009.10	3013.10	3001.90	3005.40	3009.40	2988.30	3036.40	3070.20	3033.00	3041.20
VSCF	3017.80	3024.20	3024.20	3013.50	3002.70	3008.00	3012.40	2992.70	3052.00	3081.90	3055.20	3052.80

Table S7 Harmonic (HO), EHO, VSCF and VPT2 frequencies (cm^{-1}) for NH_2 antisymmetric stretching, NH_2 symmetric stretching and NH_2 bending (for target site N7H9H10), along with for CH_2 antisymmetric and symmetric stretching (for target site C1H2H3), calculated using 6-311++G(2*df,2p*) (**H1P**), 6-31G(*d*) (**S1P**) and different combinations of ASHBS approach using two distinct layers of acrylamide (**M1**) molecule.

NH_2 Antisymmetric Stretch												
	B3PW91				**B3LYP**				**MP2**			
	H1P	**S1P**	$L_1^a(M1)$	$L_2^a(M1)$	**H1**	**S2**	$L_1^a(M1)$	$L_2^a(M1)$	**H1**	**S2**	$L_1^a(M1)$	$L_2^a(M1)$
HO	3753.33	3749.44	3758.64	3754.27	3729.69	3716.52	3731.39	3730.59	3781.73	3753.37	3776.33	3778.99
VPT2	3555.39	3664.17	3303.42	3537.78	3529.21	3585.32	3648.62	3502.45	3673.64	3602.02	3631.13	3640.41
EHO	3561.80	3552.50	3564.10	3562.60	3538.00	3519.10	3537.90	3538.90	3587.50	3561.60	3582.70	3585.90
VSCF	3563.30	3553.10	3565.00	3564.10	3539.50	3519.70	3538.80	3540.20	3590.50	3563.00	3584.60	3588.70
NH_2 Symmetric Stretch												
	B3PW91				**B3LYP**				**MP2**			
	H1P	**S1P**	$L_1^a(M1)$	$L_2^a(M1)$	**H1P**	**S1P**	$L_1^a(M1)$	$L_2^a(M1)$	**H1P**	**S1P**	$L_1^a(M1)$	$L_2^a(M1)$
HO	3619.21	3619.44	3624.33	3620.31	3598.98	3591.58	3601.51	3600.11	3635.70	3619.08	3638.84	3635.04
VPT2	3445.06	3532.11	3263.56	3432.54	3423.36	3467.97	3510.80	3404.59	3523.22	3480.70	3501.01	3501.52
EHO	3434.60	3433.10	3438.80	3434.80	3414.10	3404.70	3417.30	3414.50	3444.30	3431.40	3446.70	3443.10
VSCF	3465.30	3464.10	3469.40	3465.60	3444.90	3436.10	3448.00	3445.30	3476.20	3462.80	3478.50	3475.00
NH_2 Bend												
	B3PW91				**B3LYP**				**MP2**			
	H1P	**S1P**	$L_1^a(M1)$	$L_2^a(M1)$	**H1P**	**S1P**	$L_1^a(M1)$	$L_2^a(M1)$	**H1P**	**S1P**	$L_1^a(M1)$	$L_2^a(M1)$
HO	1616.04	1646.57	1619.09	1616.00	1620.55	1646.18	1623.45	1620.10	1621.16	1664.70	1631.10	1621.91
VPT2	1575.95	1587.71	1597.69	1578.56	1579.85	1597.18	1573.40	1583.58	1565.69	1619.62	1588.63	1575.55
EHO	1589.80	1619.80	1593.00	1589.80	1593.50	1619.50	1597.00	1593.00	1595.20	1637.50	1604.80	1596.30
VSCF	1590.10	1620.20	1593.40	1590.20	1593.80	1619.80	1597.40	1593.20	1595.50	1637.90	1605.10	1596.50
CH_2 Antisymmetric Stretch												
	B3PW91				**B3LYP**				**MP2**			
	H1P	**S1P**	$L_1^b(M1)$	$L_2^b(M1)$	**H1P**	**S1P**	$L_1^b(M1)$	$L_2^b(M1)$	**H1P**	**S1P**	$L_1^b(M1)$	$L_2^b(M1)$
HO	3246.97	3276.86	3249.54	3247.56	3237.60	3265.06	3239.92	3237.80	3302.99	3323.92	3305.52	3304.02
VPT2	3111.59	3138.46	3119.13	3119.82	3104.29	3125.04	3102.71	3106.18	3159.85	3183.99	3163.77	3161.43
EHO	3077.60	3100.30	3080.90	3077.40	3067.40	3086.70	3069.50	3067.10	3129.30	3148.10	3132.00	3129.90
VSCF	3078.10	3100.20	3081.50	3077.80	3067.40	3086.70	3069.70	3067.10	3130.00	3147.90	3132.60	3130.70
CH_2 Symmetric Stretch												
	B3PW91				**B3LYP**				**MP2**			
	H1P	**S1P**	$L_1^b(M1)$	$L_2^b(M1)$	**H1P**	**S1P**	$L_1^b(M1)$	$L_2^b(M1)$	**H1P**	**S1P**	$L_1^b(M1)$	$L_2^b(M1)$
HO	3148.84	3170.93	3153.34	3148.70	3142.95	3161.33	3148.15	3142.73	3194.97	3216.29	3200.41	3196.88
VPT2	2986.67	3005.14	2999.68	2984.81	2971.74	2998.52	2992.18	2971.60	3019.80	3034.55	3037.90	3031.24
EHO	3017.50	2993.00	3011.50	3015.20	3002.30	2965.60	3007.50	2999.50	3051.90	3069.40	3054.80	3054.00
VSCF	3018.60	3007.80	3027.80	3015.80	3003.20	2989.30	3020.90	3001.00	3066.00	3385.50	3070.50	3067.80

Table S7a VPT2 frequencies (cm^{-1}) for NH_2 antisymmetric and NH_2 symmetric stretching (for target site N7H9H1)calculated using **H1P** (6-311++G(2*df,2p*)) and four ASHBS combinations: **C5** (6-311++G(2*df,2p*)/6-31G(*d*)), **C6** (6-311++G(2*df,2p*)/6-31G(*d,p*)), **C7** (6-311++G(2*df,2p*)/6-311G(*d*)) and **C8** (6-311++G(2*df,2p*)/6-311G(*d,p*)) using B3PW91 method, for acrylamide (**M1**) molecule at layer 1 ($L_1^a(M1)$).

NH_2 antisymmetric stretching					
Basis Set	**H1P**	**C5**	**C6**	**C7**	**C8**
VPT2	3555.3	3303.4	3407.5	3533.9	3536.5
NH_2 symmetric stretching					
VPT2	3445.1	3263.6	3338.8	3430.7	3432.4

Table S8 EHO, VSCF and VPT2 frequencies (cm^{-1}) for NH (N16H13) and CO (C8O14) stretching (for t and t' target site), calculated using def2-TZVP (**H2**), def2-SV (**S2**), and its combination of ASHBS approach using distinct layers of Isatin (**M2**) molecule.

NH stretch						
Methods	**H2**	L^{t}_{NH}**(M2)**	L^{t}_{NHC}**(M2)**	$L^{t}_{NHC'}$**(M2)**	$L^{t}_{NHCC'}$**(M2)**	**S2**
EHO	3300.2	3250.5	3305.0	3305.7	3300.3	3249.2
VSCF	3372.9	3326.4	3377.5	3378.3	3373.0	3323.9
VPT2	3474.0	3481.3	3478.5	3479.9	3474.4	3423.3
CO stretch						
Methods	**H2**	$L^{t'}_{CO}$**(M2)**	$L^{t'}_{CON}$**(M2)**	$L^{t'}_{COC''}$**(M2)**	$L^{t'}_{CONC''}$**(M2)**	**S2**
EHO	1817.8	1839.0	1815.2	1820.6	1817.8	1863.2
VSCF	1822.7	1845.0	1821.0	1825.7	1823.2	1868.7
VPT2	1817.3	1818.3	1813.5	1820.4	1824.7	1870.6

Table S8a Cubic and Quartic force constant (cm^{-1}) values considering the coupling of C8O14 stretching (mode **6**) with adjacent C7O15 stretching (mode **7**), considering def2-TZVPP basis set.

Cubic force constant (f_{ijk})		**Quartic force constant (f_{ijkl})**	
f_{666}	-469.26	f_{6666}	151.16
f_{766}	-172.05	f_{7666}	38.10
f_{776}	100.04	f_{7766}	23.54
f_{777}	-517.06	f_{7776}	-39.17
		f_{7777}	158.79

Table S9 Harmonic (HO)**,** EHO, VSCF and VPT2 frequencies (cm^{-1}) as well as harmonic (I_{HO}) and anharmonic (I_{AO}) intensities (km mol^{-1}) for CO (C8O14) stretching (for H13N16C8O14C7O15 target site), calculated using def2-TZVPP (**H1**), def2-TZVP (**H2**), def2-SVP (**S1**), def2-SV (**S2**), and different combinations of ASHBS approach using two distinct layers of isatin (**M2**) molecule.

C1 (def2-TZVPP & def2-SV)				
	H1	$L_1^a(M2)$	$L_2^a(M2)$	**S2**
HO	1850.8	1851.5	1850.6	1896.4
EHO	1817.5	1821.9	1820.7	1863.2
VSCF	1822.5	1827.0	1825.7	1868.7
VPT2	1816.8	1829.8	1829.1	1870.6
I_{HO}	285.9	281.3	283.5	293.7
I_{AO}	117.3	104.9	71.6	211.4
C2 (def2-TZVP & def2-SV)				
	H2	$L_1^a(M2)$	$L_2^a(M2)$	**S2**
HO	1850.8	1851.5	1850.6	1896.4
EHO	1817.8	1821.6	1820.8	1863.2
VSCF	1822.7	1826.6	1825.8	1868.7
VPT2	1817.3	1829.0	1829.2	1870.6
I_{HO}	287.2	282.3	284.6	293.7
I_{AO}	131.1	122.2	72.7	211.4
C3 (def2-TZVPP & def2-SVP)				
	H1	$L_1^a(M2)$	$L_2^a(M2)$	**S1**
HO	1850.8	1851.5	1850.6	1895.4
EHO	1817.5	1822.1	1820.2	1862.4
VSCF	1822.5	1827.1	1825.1	1867.8
VPT2	1816.8	1828.7	1827.5	1868.7
I_{HO}	285.9	281.0	283.2	288.5
I_{AO}	117.3	143.5	100.1	225.1
C4 (def2-TZVP & def2-SVP)				
	H2	$L_1^a(M2)$	$L_2^a(M2)$	**S1**
HO	1850.8	1851.5	1850.5	1895.4
EHO	1817.8	1821.8	1820.2	1862.4
VSCF	1822.7	1826.8	1825.1	1867.8
VPT2	1817.3	1828.1	1827.6	1868.7
I_{HO}	287.2	282.1	284.4	288.5
I_{AO}	131.1	147.5	95.7	225.1

Table S9a Percentage error for CO (C8O14) stretching calculated by considering the low basis and ASHBS approaches across four combinations, using the corresponding high basis results of each combination as the reference to evaluate the error for the three anharmonic vibrational algorithms.

C1 (def2-TZVPP/def2-SV), Reference is H1			
	S2	$L_1^a(M2)$	$L_2^a(M2)$
EHO	2.51	0.24	0.18
VSCF	2.53	0.25	0.18
VPT2	2.96	0.72	0.68
C2 (def2-TZVP/def2-SV), Reference is H2			
	S2	$L_1^a(M2)$	$L_2^a(M2)$
EHO	2.50	0.21	0.17
VSCF	2.52	0.21	0.17
VPT2	2.93	0.64	0.65
C3 (def2-TZVPP/def2-SVP), Reference is H1			
	S1	$L_1^a(M2)$	$L_2^a(M2)$
EHO	2.47	0.25	0.15
VSCF	2.49	0.25	0.14
VPT2	2.86	0.66	0.59
C4 (def2-TZVP/def2-SVP), Reference is H2			
	S1	$L_1^a(M2)$	$L_2^a(M2)$
EHO	2.45	0.22	0.13
VSCF	2.47	0.22	0.13
VPT2	2.83	0.59	0.57

Table S10 Harmonic (HO)**,** EHO, VSCF and VPT2 frequencies (cm^{-1}) as well as harmonic (I_{HO}) and anharmonic intensities (I_{AO}) (km mol^{-1}) for CO (C7O15) stretching (for H13N16C8O14C7O15 target site), calculated using def2-TZVPP (**H1**), def2-TZVP (**H2**), def2-SVP (**S1**), def2-SV (**S2**), and different combinations of ASHBS approach using two distinct layers of isatin (**M2**) molecule.

C1 (def2-TZVPP & def2-SV)				
	H1	$L_1^a(M2)$	$L_2^a(M2)$	**S2**
HO	1830.3	1830.3	1830.7	1870.4
EHO	1797.0	1796.2	1798.8	1836.8
VSCF	1803.1	1802.3	1805.0	1843.1
VPT2	1794.8	1793.7	1795.9	1841.1
I_{HO}	373.9	362.8	365.5	340.9
I_{AO}	209.8	179.6	171.4	96.2
C2 (def2-TZVP & def2-SV)				
	H2	$L_1^a(M2)$	$L_2^a(M2)$	**S2**
HO	1830.3	1830.3	1830.7	1870.4
EHO	1795.3	1795.5	1798.9	1836.8
VSCF	1801.4	1801.7	1805.0	1843.1
VPT2	1792.8	1793.2	1795.9	1841.1
I_{HO}	373.4	362.7	365.4	340.9
I_{AO}	176.0	178.7	172.0	96.2
C3 (def2-TZVPP & def2-SVP)				
	H1	$L_1^a(M2)$	$L_2^a(M2)$	**S1**
HO	1830.3	1830.2	1830.7	1870.3
EHO	1797.0	1796.4	1798.4	1836.6
VSCF	1803.1	1802.6	1804.4	1843.0
VPT2	1794.8	1793.4	1795.1	1841.8
I_{HO}	373.9	364.4	367.3	345.1
I_{AO}	209.8	169.5	130.4	97.1
C4 (def2-TZVP & def2-SVP)				
	H2	$L_1^a(M2)$	$L_2^a(M2)$	**S1**
HO	1830.3	1830.3	1830.7	1870.3
EHO	1795.3	1795.8	1798.4	1836.6
VSCF	1801.4	1801.9	1804.5	1843.0
VPT2	1792.8	1792.9	1795.0	1841.8
I_{HO}	373.4	364.3	367.1	345.1
I_{AO}	176.0	169.7	132.3	97.1

Table S10a Percentage error for CO (C7O15) stretching calculated by considering the low basis and ASHBS approaches across four combinations, using the corresponding high basis results of each combination as the reference to evaluate the error for the three anharmonic vibrational algorithms.

C1 (def2-TZVPP/def2-SV), Reference is H1			
	S2	$L_1^a(M2)$	$L_2^a(M2)$
EHO	2.21	0.04	0.10
VSCF	2.22	0.04	0.11
VPT2	2.58	0.06	0.06
C2 (def2-TZVP/def2-SV), Reference is H2			
	S2	$L_1^a(M2)$	$L_2^a(M2)$
EHO	2.31	0.01	0.20
VSCF	2.31	0.02	0.20
VPT2	2.73	0.03	0.18
C3 (def2-TZVPP/def2-SVP), Reference is H1			
	S1	$L_1^a(M2)$	$L_2^a(M2)$
EHO	2.20	0.03	0.08
VSCF	2.21	0.03	0.07
VPT2	2.62	0.08	0.02

C4 (def2-TZVP/def2-SVP), Reference is H2			
	S1	$L_1^a(M2)$	$L_2^a(M2)$
EHO	2.30	0.03	0.17
VSCF	2.31	0.03	0.17
VPT2	2.73	0.01	0.13

Table S11 Harmonic (HO)**,** EHO, VSCF and VPT2 frequencies (cm^{-1}) as well as harmonic (I_{HO}) and anharmonic intensities (I_{AO}) ($km\ mol^{-1}$) for NH (N16H13) bending (for H13N16C8O14C7O15 target site), calculated using def2-TZVPP (**H1**), def2-TZVP (**H2**), def2-SVP (**S1**), def2-SV (**S2**), and different combinations of ASHBS approach using two distinct layers of issatin (**M2**) molecule.

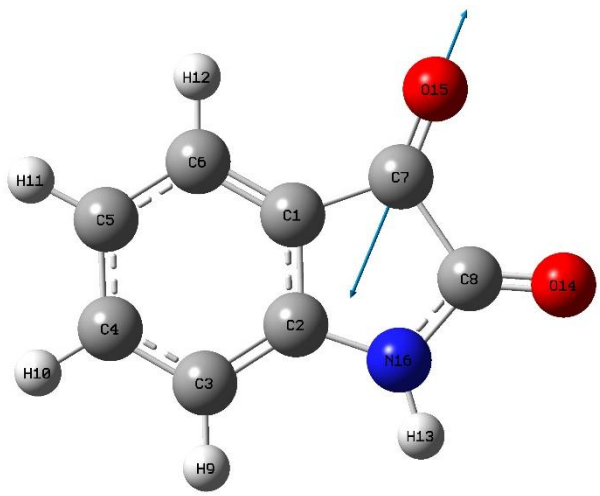
C1 (def2-TZVPP & def2-SV)				
	H1	$L_1^a(M2)$	$L_2^a(M2)$	**S2**
HO	1413.7	1425.8	1422.5	1435.9
EHO	1396.0	1409.2	1405.4	1419.1
VSCF	1395.2	1408.7	1404.9	1418.5
VPT2	1384.6	1395.3	1393.3	1409.1
I_{HO}	41.9	36.0	34.6	33.2
I_{AO}	17.8	27.5	24.7	5.1
C2 (def2-TZVP & def2-SV)				
	H2	$L_1^a(M2)$	$L_2^a(M2)$	**S2**
HO	1413.5	1426.5	1422.3	1435.9
EHO	1396.9	1410.3	1405.7	1419.1
VSCF	1396.0	1409.8	1405.1	1418.5
VPT2	1384.3	1396.5	1393.8	1409.1
I_{HO}	41.8	36.3	35.0	33.2
I_{AO}	11.6	26.3	26.4	5.1
C3 (def2-TZVPP & def2-SVP)				
	H1	$L_1^a(M2)$	$L_2^a(M2)$	**S1**
HO	1413.7	1423.5	1420.4	1429.3
EHO	1396.0	1406.9	1402.7	1412.9
VSCF	1395.2	1406.4	1402.1	1412.5
VPT2	1384.6	1393.5	1391.5	1396.2
I_{HO}	41.9	33.1	32.1	31.6
I_{AO}	17.8	24.3	20.0	14.7
C4 (def2-TZVP & def2-SVP)				
	H1	$L_1^a(M2)$	$L_2^a(M2)$	**S1**
HO	1413.5	1424.2	1420.2	1429.3
EHO	1396.9	1408.2	1403.2	1412.9
VSCF	1396.0	1407.6	1402.6	1412.5
VPT2	1384.3	1394.8	1391.9	1396.2
I_{HO}	41.8	33.4	32.5	31.6
I_{AO}	11.6	23.2	21.5	14.7

Table S11a Percentage error for NH bending calculated by considering the low basis and ASHBS approaches across four combinations, using the corresponding high basis results of each combination as the reference to evaluate the error for the three anharmonic vibrational algorithms.

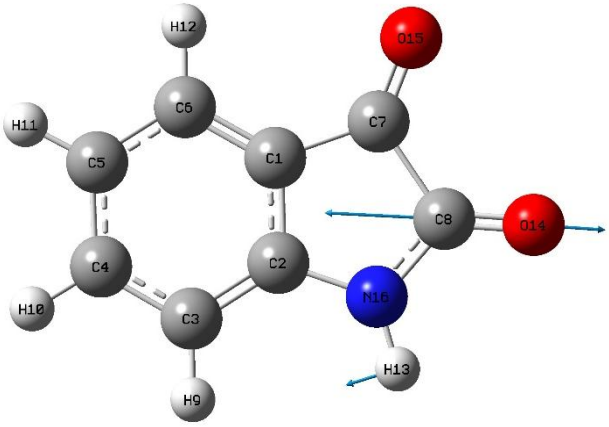
C1 (def2-TZVPP/def2-SV), Reference is H1			
	S2	$L_1^a(M2)$	$L_2^a(M2)$
EHO	1.65	0.95	0.67
VSCF	1.67	0.97	0.70
VPT2	1.77	0.78	0.63
C2 (def2-TZVP/def2-SV), Reference is H2			
	S2	$L_1^a(M2)$	$L_2^a(M2)$
EHO	1.59	0.96	0.63
VSCF	1.61	0.99	0.65
VPT2	1.79	0.88	0.69
C3 (def2-TZVPP/def2-SVP), Reference is H1			
	S1	$L_1^a(M2)$	$L_2^a(M2)$
EHO	1.21	0.78	0.48
VSCF	1.24	0.80	0.49
VPT2	0.84	0.65	0.50
C4 (def2-TZVP/def2-SVP), Reference is H2			
	S1	$L_1^a(M2)$	$L_2^a(M2)$
EHO	1.15	0.81	0.45
VSCF	1.18	0.83	0.47
VPT2	0.86	0.76	0.55

Table S12 CPU time in hours required to calculate the QFF of the isatin (**M2**) molecule using def2-TZVPP (**H1**), def2-TZVP (**H2**), def2-SVP (**S1**), def2-SV (**S2**), and different combinations of ASHBS approach employing two distinct layers, using Intel Xeon Platinum 8268 processors, with 20 processors operating in parallel.

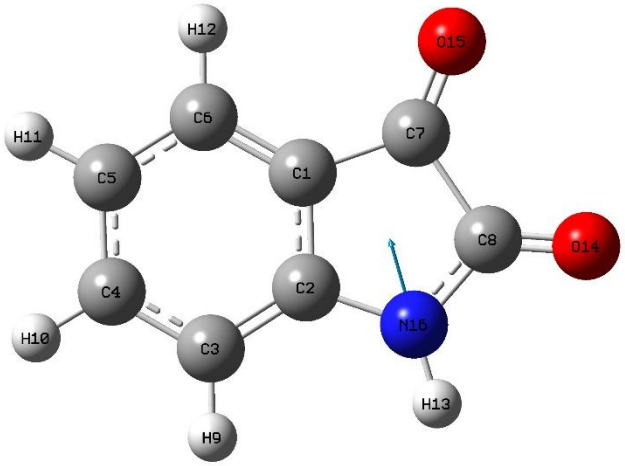
H1	**H2**	**S1**	**S2**
15.66	12.53	1.70	1.52
$L_1^a(M2)$			
C1	**C2**	**C3**	**C4**
3.92	3.81	4.37	3.88
$L_2^a(M2)$			
C1	**C2**	**C3**	**C4**
5.56	5.51	7.19	5.67



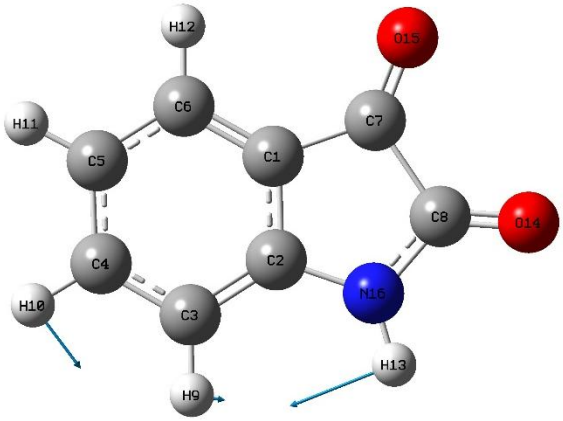
a) C7O15 stretch



b) C8O14 stretch



c) N16H13 stretch



d) N16H13 bend

Figure S1 Graphical representation of target modes of isatin

Section S1: References

1. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652.
2. C. Møller and M. S. Plesset, *Phys. Rev.*, 1934, **46**, 618-622.
3. J. P. Perdew and Y. Wang, *Phys. Rev. B*, 1992, **45**, 13244-13249.
4. R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650-654.
5. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297-3305.
6. J. Bloino and V. Barone, *J. Chem. Phys.*, 2012, **136**, 124108.