

Supplementary Information: A quantum dynamics investigation of the photostability of pyrazine

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S1 Parameters of the diabatic model potential

We provide here the values of the parameters entering the definition of the model Hamiltonian used in the paper. The Hamiltonian reads

$$H_0(Q) = \sum_i \frac{\omega_i}{2} \left(-\frac{\partial^2}{\partial Q_i^2} + Q_i^2 \right) I + W(Q). \quad (1)$$

The diagonal and non-diagonal elements of the diabatic potential matrix $W(Q)$ read

$$W_{\alpha\alpha}(Q) = E_\alpha + \sum_i \kappa_i^{(\alpha)} Q_i + \sum_{i,j} \gamma_{ij}^{(\alpha)} Q_i Q_j + \sum_{i,j} \sigma_{ij}^{(\alpha)} Q_i^2 Q_j + \sum_i \eta_i^{(\alpha)} Q_i^4 \quad (2)$$

and

$$W_{\alpha\alpha'}(Q) = \sum_i \lambda_i^{(\alpha\alpha')} Q_i + \sum_{i,j} \mu_{ij}^{(\alpha\alpha')} Q_i Q_j + \sum_{i,j} \theta_{ij}^{(\alpha\alpha')} Q_i^2 Q_j, \quad (3)$$

respectively.

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S1.1 Diagonal bilinear parameters

Table S1 Diagonal bilinear parameters $\gamma_{ij}^{(\alpha)}$.

	GS	$B_{3u}(n\pi^*)$	$A_u(n\pi^*)$	$B_{2u}(\pi\pi^*)$
γ_{6a6a}	0.0056	0.0012	0.0090	-0.0077
γ_{6a1}	-0.0056	-0.0020	0.0019	-0.0122
γ_{6a9a}	-0.0004	-0.0043	-0.0076	0.0026
γ_{6a8a}	-0.0172	-0.0147	-0.0088	-0.0212
γ_{11}	0.0190	0.0016	0.0014	0.0037
γ_{19a}	-0.0114	-0.0073	0.0004	-0.0046
γ_{18a}	-0.0490	-0.0351	-0.0276	-0.0364
γ_{9a9a}	0.0009	-0.0034	-0.0033	0.0007
γ_{9a8a}	-0.0159	-0.0128	-0.0086	-0.0160
γ_{8a8a}	-0.0012	-0.0097	-0.0192	-0.0057
γ_{10a10a}	0.0081	-0.0157	-0.0464	-0.0101
γ_{44}	-0.0070	-0.0321	-0.0309	-0.0318
γ_{45}	-0.0001	0.0041	0.0124	-0.0226
γ_{55}	-0.0016	-0.0167	-0.0293	-0.0207
γ_{8b8b}	0.0450	-0.0106	0.0020	0.0150
γ_{16a16a}	0.0030	0.0116	-0.0092	-0.0279
γ_{16a17a}	0.0016	0.0185	0.0205	0.0059
γ_{17a17a}	0.0010	-0.0203	-0.0403	-0.0250

S1.2 Non-diagonal bilinear parameters

Table S2 Non-diagonal bilinear parameters $\mu_{ij}^{(\alpha\alpha')}$.

	$GS/A_u(n\pi^*)$	$B_{3u}(n\pi^*)/A_u(n\pi^*)$	$B_{3u}(n\pi^*)/B_{2u}(\pi\pi^*)$	$A_u(n\pi^*)/B_{2u}(\pi\pi^*)$
μ_{6a16a}	0.00151	μ_{6a8b} 0.00478	μ_{6a10a} 0.00364	μ_{6a4} 0.00601
μ_{116a}	0.00075	μ_{18b} -0.00006	μ_{110a} -0.01126	μ_{14} 0.00054
μ_{8a16a}	0.00419	μ_{8a8b} 0.00874	μ_{8a10a} 0.00823	μ_{8a4} -0.00710
μ_{9a16a}	0.00064	μ_{9a8b} -0.00032	μ_{9a10a} 0.00206	μ_{9a4} -0.00067
μ_{6a17a}	0.00119	μ_{10a4} 0.00555	μ_{48b} -0.01263	μ_{6a5} 0.01096
μ_{117a}	0.00059	μ_{10a5} -0.01890	μ_{58b} 0.00219	μ_{15} 0.00464
μ_{8a17a}	0.00330			μ_{8a5} -0.00373
μ_{9a17a}	0.00050			μ_{9a5} 0.00437
				μ_{10a8b} -0.01612

S1.3 Diagonal third and fourth order parameters

Table S3 Diagonal third and fourth order parameters $\sigma_{ij}^{(\alpha)}$ and $\sum_i \eta_i^{(\alpha)}$.

	GS	$B_{3u}(n\pi^*)$	$A_u(n\pi^*)$	$B_{2u}(\pi\pi^*)$
σ_{6a6a}	0.000055	-0.000104	-0.000081	-0.000364
σ_{6a1}	-0.000117	-0.000048	-0.000072	-0.000053
σ_{6a8a}	-0.000148	-0.000140	-0.000161	-0.000266
σ_{6a9a}	-0.000081	-0.000066	-0.000063	-0.000108
σ_{11}	-0.000758	-0.002112	-0.002080	-0.001870
σ_{16a}	-0.000020	-0.000008	-0.000011	0.000001
σ_{18a}	-0.000114	-0.000055	-0.000066	-0.000068
σ_{19a}	-0.000014	0.000004	0.000009	0.000006
σ_{8a8a}	-0.000048	-0.001441	0.001309	-0.000303
σ_{8a6a}	-0.000201	-0.000224	-0.000282	-0.000388
σ_{8a1}	-0.000375	-0.000341	-0.000334	-0.000456
σ_{8a9a}	-0.000398	-0.000223	-0.000123	-0.000361
σ_{9a9a}	0.000013	-0.000488	-0.000174	0.000088
σ_{9a6a}	-0.000043	-0.000061	-0.000046	-0.000064
σ_{9a1}	-0.000081	-0.000063	-0.000079	-0.000054
σ_{9a8a}	-0.000105	-0.000075	-0.000080	-0.000107
η_{6a}	-0.0002525	-0.0000270	-0.0000908	-0.0002189
η_1	-0.0001893	0.0000017	0.0000824	-0.0000159
η_{8a}	-0.0002329	-0.0001183	-0.0002443	-0.0001635
η_{9a}	-0.0001044	0.0001256	0.0000665	0.0000878
η_{10a}	0.0002722	0.0008554	0.0010884	0.0004107
η_4	-0.0000171	0.0002530	0.0001441	0.0002722
η_5	0.0003306	0.0007727	0.0007324	0.0009539
η_{8b}	0.0000546	-0.0002574	0.0004438	-0.0004234
η_{16a}	0.0003349	-0.0003647	0.0006847	-0.0003633
η_{17a}	0.0001776	-0.0003146	0.0002099	-0.0003036

S1.4 Non-diagonal third order parameters

Table S4 Non-diagonal third order parameters $\theta_{ij}^{(\alpha\alpha')}$.

	$GS/A_u(n\pi^*)$	$B_{3u}(n\pi^*)/A_u(n\pi^*)$	$B_{3u}(n\pi^*)/B_{2u}(\pi\pi^*)$	$A_u(n\pi^*)/B_{2u}(\pi\pi^*)$
θ_{16a16a}	0.000090	θ_{8b8b} -0.000723	θ_{10a10a} -0.000705	θ_{44} -0.000831
θ_{17a17a}	0.000033			θ_{55} -0.001088
θ_{6a16a}	0.000042			
θ_{116a}	0.000010			
θ_{8a16a}	0.000320			
θ_{9a16a}	0.000007			
θ_{6a17a}	0.000030			
θ_{117a}	0.000007			
θ_{8a17a}	0.000232			
θ_{9a17a}	0.000005			

S2 Internal conversion to the $A_u(n\pi^*)$ state

In this section, we investigate the influence of the relative energy of the $B_{2u}(\pi\pi^*)$ and $A_u(n\pi^*)$ states on the efficiency of the internal conversion to the $A_u(n\pi^*)$ state observed in our calculations. We perform 100 fs wavepacket propagation using our model Hamiltonian and considering two values of 4.8 and 5.0 eV for the $A_u(n\pi^*)$ state vertical excitation energy. The first value is the value used in the present work. Using the second value, the $A_u(n\pi^*)$ state lies 0.21 eV above the $B_{2u}(\pi\pi^*)$ state. In these calculations, a vertical excitation is assumed, *i.e.* the initial wavepacket is the the ground vibronic wavefunction projected on the diabatic $B_{2u}(\pi\pi^*)$ state vibronic manifold. The diabatic electronic state populations obtained from these calculations are shown in Fig. S1 below.

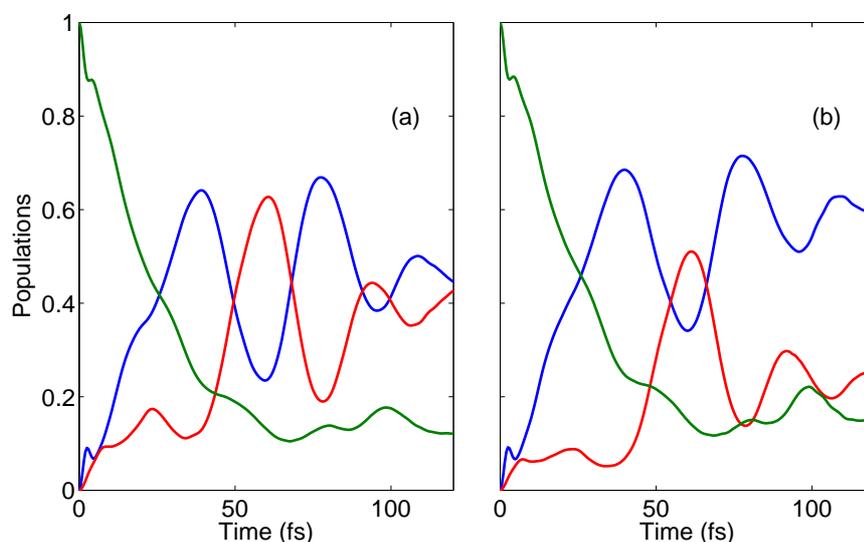


Fig. S1 Populations of the $B_{3u}(n\pi^*)$ (blue), $A_u(n\pi^*)$ (red) and $B_{2u}(\pi\pi^*)$ (green) diabatic electronic states using a value of (a) 4.8 eV and (b) 5.0 eV for the $A_u(n\pi^*)$ state vertical excitation energy.

We can see that the calculation performed with a $A_u(n\pi^*)$ state vertical excitation energy of 5.0 eV yields an only slightly less efficient internal conversion to the $A_u(n\pi^*)$ state despite the fact that in this calculation the $A_u(n\pi^*)$ state is higher in energy than the $B_{2u}(\pi\pi^*)$ state at the Franck-Condon geometry. These results provide further evidence that the $A_u(n\pi^*)$ state needs to

be taken into account to correctly describe the dynamics of photoexcited pyrazine. In addition, these calculations show a rather different electronic state dynamics than the calculations performed in the main text including explicitly the excitation pulse. This illustrates the importance of accounting for the excitation pulse when simulating time-resolved experiments.