Supporting Information for "Gas-Phase Cytosine and Cytosine-N$_1$-Derivatives Have 0.1 - 1 Nanosecond Lifetimes Near the S_1 State Minimum"

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Lifetime fits

The S_1 ($^1\pi\pi^*$) state population is fitted to the following model

$$\frac{d[S_1]}{dt} = -(k_{IC,v}^{S_1} + k_{ISC,v}^{S_1} + k_{rad}^{S_1}) \cdot [S_1] \tag{1}$$

where the first term is the $S_1 \rightarrow S_0$ radiative decay rate k_{rad}. The SCS-CC2/aug-cpVDZ calculated radiative lifetimes $\tau_{rad} = k_{rad}^{-1}$ of cytosine, N$_1$-methylcytosine, N$_1$-ethylcytosine and N$_1$-isopropylcytosine are given in Table S1. The S_1 state is assumed to decay nonradiatively to S_0 by internal conversion (IC) with the rate $k_{IC}^{S_1}$ and in parallel to the triplet T_1 state with the intersystem crossing (ISC) rate constant $k_{ISC}^{S_1}$. Since the lowest $^1n\pi^*$ state is calculated to lie above the lowest $^1\pi\pi^*$ state with the SCS-CC2 method, we do not consider it in the relaxation pathway model.

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However, should the ${}^1n\pi^*$ lie below the ${}^1\pi\pi^*$ state, e.g., for N_1-isopropylcytosine, the transients do not exclude a relaxation mechanism ${}^1\pi\pi^* \rightsquigarrow {}^1n\pi^* \rightsquigarrow S_0$, in which the ${}^1n\pi^* \rightsquigarrow S_0$ relaxation is much faster than the ${}^1\pi\pi^* \rightsquigarrow {}^1n\pi^*$ rate. In this case, the $k_{IC}^{S_1}$ rate constant would characterize the ${}^1\pi\pi^* \rightsquigarrow {}^1n\pi^*$ internal conversion.

The lifetimes indicated in Fig. 2, Figures S1 to S3 and given in Table S1 are $\tau = (k_{IC}^{S_1} + k_{rad}^{S_1} + k_{ISC}^{S_1})^{-1}$, corresponding to the exponential decay of the S_1 state in eqn.(1). The T_1 state is populated with the rate $k_{ISC}^{S_1}$ and relaxes to S_0 by $T_1 \rightsquigarrow S_0$ ISC as well as by phosphorescence; these pathways are combined into one constant $k_T = k_{ISC}^{T_1} + k_{phos}$:

$$\frac{d[T_1]}{dt} = k_{ISC}^{S_1} \cdot [S_1] - k_T \cdot [T_1] \tag{2}$$

The ns excitation/ionization transients (for cytosine, see ref. 1) show that the T_1 decay is on the $\sim$ 200 ns timescale, so k_T is small compared to the other rates and is set to zero for the fits. Using the calculated k_{rad}, the rate constants $k_{ISC}^{S_1}$ and $k_{IC}^{S_1}$ are least-squares fitted to the observed transients.

The ps pump/ionization transients were fitted using a program written in IDL, which employs a Levenberg-Marquardt nonlinear least-squares fit of the transient ion signal to eqns.(1) and (2). This decay model is then convoluted with the instrument response function (IRF), which accounts for the convolution of the pulse widths of the pump and ionisation lasers. The IRF was determined from the rise of the decay curve and can be represented by a Gaussian with a full width at half-maximum (FWHM) of 20 ps.

We note that the fitted values of k_{IC} and k_{ISC} are based on the assumption that the ionization cross sections ($\sigma_{ion}(S_1)$,$\sigma_{ion}(T_1)$) for the S_1 and triplet states are equal. For cytosine, the ratio of cross-sections has been estimated to be $\sigma_{ion}(S_1)/\sigma_{ion}(T_1) \sim 3$ at the ionization wavelength of 215 nm.[1] For the N_1-substituted cytosines the ratio has not yet been calculated, we estimate it to be between $\sigma_{ion}(S_1)/\sigma_{ion}(T_1) \sim 1-2$. Thus the k_{IC} and k_{ISC} values given in Table S1 must be only considered as indicative, and an improved treatment might increase the k_{ISC} by up to 3x.

Table S1: Excited state lifetimes τ of S_1 state keto-amino cytosine, N_1-methylcytosine, N_1-ethylcytosine and N_1-isopropylcytosine, as a function of vibrational level v, calculated radiative lifetimes and selected k_{IC} and k_{ISC} values.

	Transition[a]	Exp. lifetime τ [b] S_1/ ps	τ_{rad} [c] $S_1 \rightarrow S_0$/ ns	$k_{IC,v}^{S_1}$ [d] s^{-1}	$k_{ISC,v}^{S_1}$ [e] s^{-1}
Cytosine	0_0^0	730 ± 60	18.7	$1.2 \cdot 10^9$	$1.0 \cdot 10^8$
	$0_0^0 + 92$	460 ± 50			
N_1-Methylcytosine	$0_0^0 + 66$	600 ± 290	12.5	$1.2 \cdot 10^9$	$4 \cdot 10^8$
	+201	230 ± 70			
	+274	96 ± 10			
	+297	106 ± 60			
	+339	100 ± 15			
	+372	50 ± 15			
	+401	13 ± 8			
	+429	20 ± 4			
	+460	20 ± 2			
	+516	< 20			
N_1-Ethylcytosine	0_0^0	930 ± 60	11.8	$7.9 \cdot 10^8$	$2 \cdot 10^8$
	$0_0^0 + 53$	930 ± 60			
	$+104$	1030 ± 270			
	+153	630 ± 70			
	+240	350 ± 60			
	+317	280 ± 20			
	+444	88 ± 5			
	+519	27 ± 2			
	+571	25 ± 3			
	+613	22 ± 2			
	+710	< 20			
N_1-Isopropylcytosine	$0_0^0 + 40$	100 ± 60	10.9	$9.5 \cdot 10^9$	$3.9 \cdot 10^8$
	+111	90 ± 10			
	+152	105 ± 10			
	+193	90 ± 10			
	+234	100 ± 5			
	+306	40 ± 3			
	+347	28 ± 4			

[a] In cm^{-1} relative to the respective 0_0^0 band (31835 cm^{-1} for Cyt, 31852 cm^{-1} for N_1-methyl-Cyt, 31906 cm^{-1} for N_1-ethyl-Cyt, 31786 cm^{-1} for N_1-isopropyl-Cyt
[b] Uncertainties $\pm 1\sigma$; from fitting four to eight separate transients.
[c] Radiative lifetime, calculated at the SCS-CC2/aug-cc-pVDZ level.
[d] Internal conversion rate constant, uncorrected for relative ionization cross sections, estimated error ± 50 %.
[e] Intersystem crossing rate constant, uncorrected for relative ionization cross sections, estimated error ± 100 %.

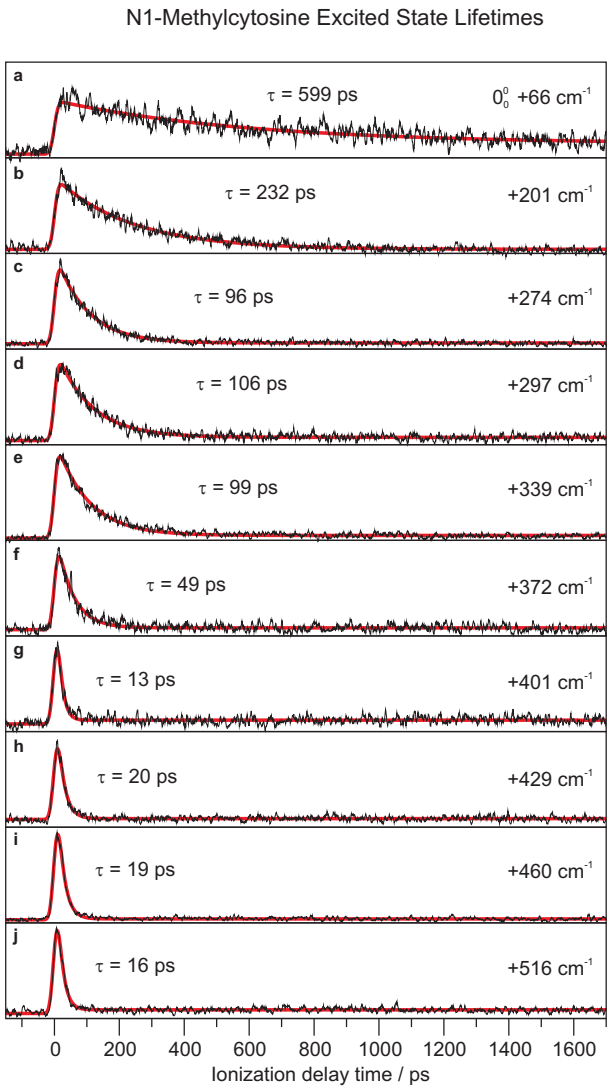

Fig. S1: Picosecond pump/delayed ionisation transients of 1-methylcytosine, as a function of vibrational excess energy from the $0_0^0 + 66$ cm^{-1} level up to $0_0^0 + 516$ cm^{-1}. The decay times are dominated by $S_1 \rightsquigarrow S_0$ internal conversion. The transients in (a), (b) and (g) exhibit minor growth contributions from $S_1 \rightsquigarrow T_1$ intersystem crossing.

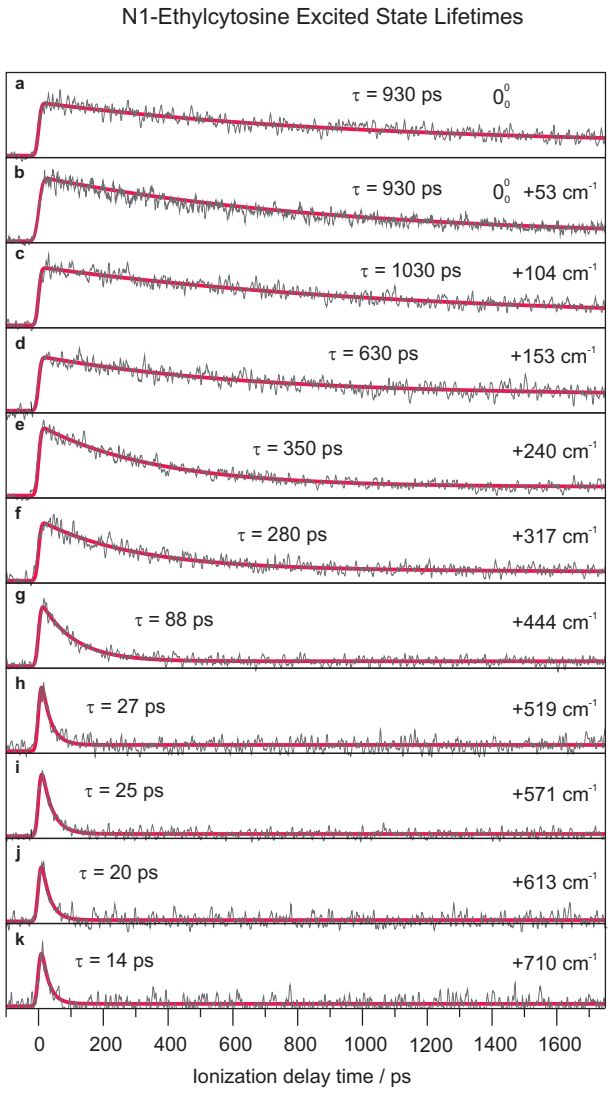

Fig. S2: Picosecond pump/delayed ionisation transients of 1-ethylcytosine, as a function of vibrational excess energy from the $v' = 0$ level up to $0_0^0 + 710$ cm^{-1}. The decay times τ are dominated by $S_1 \rightsquigarrow S_0$ internal conversion. The transients in (a), (d-h) show minor growth from $S_1 \rightsquigarrow T_1$ intersystem crossing

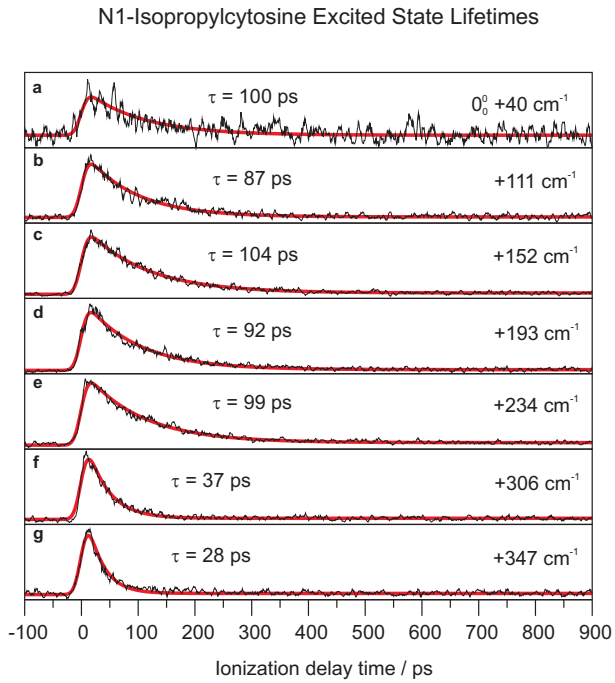

Fig. S3: Picosecond pump/delayed ionisation transients of 1-isopropylcytosine as a function of vibrational excess energy. Most transients are dominated by $S_1 \rightsquigarrow S_0$ internal conversion.The transient in (a) exhibits a small contribution from $S_1 \rightsquigarrow T_1$ intersystem crossing, see Table S1.

Table S2: SCS-CC2/aug-cc-pVDZ calculated Cartesian coordinates (in Å) of the S_0 and lowest excited $^1\pi\pi^*$ minima of amino-keto cytosine, N_1-methylcytosine and N_1-ethylcytosine, and the $^1n\pi^*$ state N_1-ethylcytosine.

S_0 state				$^1\pi\pi^*$ state				$^1n\pi^*$ state [a]			
Cytosine											
C	1.510755	0.009395	2.297425	C	1.488479	0.056142	2.179954				
N	2.654382	0.010716	1.443467	N	2.645117	-0.206218	1.464894				
C	2.580728	-0.000892	0.07691	C	2.63231	0.037881	0.067744				
C	1.352846	-0.015555	-0.537288	C	1.339701	0.043873	-0.530404				
C	0.20272	-0.013546	0.344567	C	0.208974	-0.032824	0.270747				
N	0.268585	0.003596	1.674683	N	0.296739	0.183529	1.697703				
N	-1.055394	-0.079229	-0.211137	N	-1.110484	-0.248028	-0.165473				
O	1.685213	0.020015	3.521133	O	1.727133	0.194223	3.513583				
H	3.550942	0.020198	1.921403	H	3.505724	-0.335002	1.989481				
H	3.527418	-0.000524	-0.469646	H	3.579301	0.226812	-0.438002				
H	1.259478	-0.038235	-1.624318	H	1.258689	0.102594	-1.621988				
H	-1.825888	0.100455	0.425113	H	-1.784945	0.251881	0.413964				
H	-1.178745	0.203693	-1.175726	H	-1.253696	-0.054777	-1.155616				
N_1-Methylcytosine											
N	-0.012088	-0.023294	-0.027735	N	-0.026775	0.092043	-0.004685				
C	0.00234	-0.013333	1.358961	C	0.077904	0.044842	1.29032				
N	1.280412	-0.00313	2.011758	N	1.253149	-0.061763	2.023967				
C	2.447181	-0.010384	1.299909	C	2.453658	0.254642	1.339347				
C	2.437831	-0.02979	-0.076054	C	2.42045	0.153265	-0.083539				
C	1.137239	-0.037038	-0.700071	C	1.210392	-0.065115	-0.720624				
O	-1.014596	-0.005548	2.066717	O	-1.04709	0.088593	2.043108				
N	1.051159	-0.11186	-2.075892	N	1.024714	-0.387692	-2.076767				
C	1.268955	0.016087	3.482186	C	1.265963	-0.155915	3.48659				
H	3.373322	-0.003159	1.881759	H	3.313701	0.561082	1.937101				
H	3.367394	-0.050781	-0.647709	H	3.355345	0.251062	-0.647959				
H	0.130922	0.081233	-2.459891	H	0.158618	0.009304	-2.441084				
H	1.843253	0.205464	-2.622514	H	1.820525	-0.152388	-2.667997				
H	2.309985	0.019909	3.837452	H	2.122949	-0.784137	3.775977				
H	0.740902	0.913406	3.836856	H	1.373234	0.843142	3.946295				
H	0.739571	-0.871007	3.859681	H	0.327046	-0.614189	3.825363				
N_1-Ethylcytosine											
C	1.132861	0.002326	-0.736622	C	1.213014	-0.027455	-0.788083	N	0.430142	-0.11916	0.785762
N	0.089871	0.634064	-0.201917	N	-0.013502	0.460879	-0.21386	C	1.574837	0.122921	-0.040926
C	0.027875	0.826575	1.170428	C	0.024198	0.665668	1.072781	C	1.336462	0.193606	-1.447659
N	1.141538	0.372233	1.955331	N	1.088153	0.367905	1.927522	C	0.062655	0.023774	-1.952676
C	2.198528	-0.279191	1.382951	C	2.052247	-0.54284	1.431982	N	-1.081171	-0.026374	-1.084620
C	2.250955	-0.497411	0.025395	C	2.160699	-0.647118	0.014684	C	-0.789188	-0.133418	.170554
O	-0.921735	1.373765	1.749313	O	-1.031438	1.229401	1.689106	N	-0.279099	-0.135236	-3.309091
C	1.061266	0.54187	3.420589	C	1.022489	0.645183	3.372104	O	-1.856966	-0.294407	1.043661
N	1.094544	-0.216704	-2.099358	N	1.189001	-0.066298	-2.197324	C	0.593486	-0.518360	2.195853
H	2.989793	-0.608764	2.063155	H	2.723028	-1.012881	2.15209	C	0.171858	0.577798	3.183373
H	3.092136	-1.020724	-0.432874	H	2.979776	-1.232907	-0.418011	H	2.461106	0.525074	0.457132
H	0.393384	0.320491	-2.600802	H	0.54067	0.624924	-2.572381	H	2.190786	0.351391	-2.116138
H	1.971226	-0.37488	-2.582484	H	2.108246	0.026053	-2.625377	H	-1.206584	0.239976	-3.506372
C	0.208717	-0.555094	4.068534	C	0.338973	-0.482021	4.160443	H	0.416530	0.240227	-3.951893
H	2.095186	0.525217	3.803881	H	2.065797	0.781643	3.703768	H	1.658661	-0.770496	2.312595
H	0.6258	1.533986	3.606448	H	0.479889	1.593897	3.499577	H	-0.000584	-1.434774	2.360982
H	0.159791	-0.396937	5.159395	H	0.35485	-0.246394	5.238193	H	0.366971	0.242252	4.216455
H	-0.813376	-0.524724	3.661498	H	-0.710338	-0.59026	3.840026	H	0.741924	1.503906	3.001914
H	0.644887	-1.55086	3.879374	H	0.857497	-1.442143	4.005000	H	-0.903412	0.801389	3.091703

[a] Upon rotation of the ethyl group in the S_1 state of N_1-ethylcytosine towards the molecular plane and the keto oxygen, the S_1 state character changes from pure $^1\pi\pi^*$ to nearly pure $^1n_O\pi^*$. The geometry given corresponds to the lowest energy beyond which the $^1n_O\pi^*$ character is dominant ($> 59\%$ contribution to the S_1 state). However, this is not a stationary point.

Table S3: SCS-CC2/aug-cc-pVDZ calculated Cartesian coordinates (in Å) of the S_0 state and lowest excited $^1\pi\pi^*$ and $^1n\pi^*$ state minima of keto-amino N_1-isopropylcytosine.

S_0 state				$^1\pi\pi^*$ state				$^1n\pi^*$ state			
C	1.100371	0.034632	-0.73331	C	1.134566	0.039650	-0.747939	C	1.504169	0.06581	-1.383724
N	0.0128	0.38967	-0.052906	N	0.426748	1.042771	-0.001775	C	0.354151	0.007734	-2.146683
C	0.017787	0.342489	1.333252	C	0.473282	0.905712	1.295489	N	-0.937508	-0.051253	-1.532691
N	1.258768	0.01319	1.986337	N	1.223330	-0.046331	1.995291	C	-0.912849	0.014733	-0.248218
C	2.35161	-0.373808	1.261318	C	2.280653	-0.653374	1.276645	N	0.125725	0.166409	0.62127
C	2.331638	-0.386485	-0.115089	C	2.152270	-0.683228	-0.145757	C	1.44106	0.053583	0.040204
O	-0.979207	0.582667	2.029631	O	-0.243915	1.730296	2.073120	N	0.300076	-0.145164	-3.548224
C	1.242337	-0.047441	3.474336	C	1.112266	-0.209415	3.463811	O	-2.185652	-0.053014	0.356172
N	0.99914	0.032124	-2.110858	N	0.728562	-0.042708	-2.092286	C	-0.094048	-0.125345	2.059293
H	3.239645	-0.664559	1.826209	H	3.127656	-1.054142	1.834395	C	0.029629	-1.634127	2.327972
H	3.20477	-0.700413	-0.690159	H	2.865377	-1.272927	-0.734919	C	0.854788	0.706962	2.932148
H	0.187201	0.517519	-2.480974	H	0.414840	0.862304	-2.443614	H	2.271037	0.370315	0.673256
H	1.853262	0.109554	-2.650912	H	1.427247	-0.45841	-2.706790	H	2.49008	0.085285	-1.861667
C	2.596286	0.345279	4.081004	C	2.202345	0.597882	4.189193	H	-0.559298	0.248717	-3.930497
H	0.485347	0.695948	3.763975	H	0.127147	0.209091	3.722964	H	1.116528	0.234083	-4.025299
C	0.775811	-1.438542	3.926962	C	1.144182	-1.701245	3.831126	H	-1.128383	0.203556	2.274929
H	2.464898	0.482216	5.167132	H	2.079782	0.493481	5.280802	H	0.55236	0.605003	3.987761
H	3.363743	-0.435191	3.940706	H	3.208374	0.235244	3.918307	H	1.895148	0.354177	2.845106
H	2.965276	1.29343	3.655617	H	2.129016	1.666446	3.928205	H	0.810589	1.772361	2.65423
H	0.695432	-1.472645	5.027122	H	0.904814	-1.810593	4.902527	H	-0.170994	-1.847211	3.391943
H	-0.211082	-1.66688	3.495453	H	0.398514	-2.262027	3.244649	H	-0.692193	-2.200211	1.715472
H	1.498948	-2.209643	3.60577	H	2.137725	-2.145369	3.657171	H	1.047066	-1.977133	2.079129

Table S4: SCS-CC2/aug-cc-pVDZ adiabatic and vertical $^1\pi\pi^*$ and $^1n\pi^*$ energies.

	$^1\pi\pi^*$ state	$^1n\pi^*$ state	
	adiabatic	adiabatic	vertical
Cytosine	31857		34487
N_1-Methylcytosine	31899		34724
N_1-Ethylcytosine	31966	32372[a]	34893
N_1-Isopropylcytosine	31701	31868	35051

[a] Not a minimum structure, see footnote in Table S3.

References

(1) Lobsiger, S.; Etinski, M.; Blaser, S.; Frey, H.-M.; Marian, C.; Leutwyler, S. Intersystem Crossing Rates of S_1 State Keto-Amino Cytosine at Low Excess Energy. *J. Chem. Phys.* **2015**, *143*, 234301–1–12.