Supplementary Materials: Pyrazine excited states revisited using the extended multi-state complete active space second-order perturbation method

Toru Shiozaki* and Hans-Joachim Werner†

Institut für Theoretische Chemie, Universität Stuttgart,
Pfaffenwaldring 55, D-70569 Stuttgart, Germany

Clemens Woywod‡

Centre for Theoretical and Computational Chemistry,
Department of Chemistry, University of Tromsø,
N-9037 Tromsø, Norway

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Computational details of the calculation of photoabsorption spectra

The ground state equilibrium geometry predicted by the single-state CASPT2 approach is compared to experiment in Table I and the corresponding harmonic ground state frequencies relevant for the assembly of $\hat{\mathbf{H}}_{\mathrm{vib}}$ [Table 1 in the main text] are computed as ω_1= 1026.7 (1015), ω_2=3230.6 (3055), ω_{6a}=605.0 (596), ω_{8a}=1616.6 (1582), ω_{9a}=1259.8 (1230) and ω_{10a}=926.7 (919) (the unit is cm^{-1}, experimental fundamental frequencies[1] are included in brackets). The comparison of ground state equilibrium geometry and normal frequencies indicates that the CASPT2 force field represents a reliable approximation.

The set of vibronic coupling parameters for $\hat{\mathbf{H}}_{\mathrm{vib}}$ [Table 1 in the main text] is completed by λ_{10a}=0.201 eV, $\gamma^{(1)}_{10a}$=-0.014 eV and $\gamma^{(2)}_{10a}$=-0.014 eV. The three coefficients have been determined by a least-squares fit of the eigenvalues of the two-state model potential energy matrix as a function of Q$_{10a}$ to the energies of the adiabatic 1^1B_u and 2^1B_u states (employing C_{2h} symmetry labels) obtained along Q$_{10a}$, with Q$_{6a}$=0.0, at the XMS-CASPT2 level of theory (cf. Fig. 3 of the main text).

The single-state CASPT2 electronic structure model, based on CASSCF reference functions that have been separately converged for both excited states, predicts values of 3.81 eV and 4.72 eV for the vertical excitation energies of the 1^1B_{3u} and 1^1B_{2u} states. Almost identical energy differences for the vertical $1^1A_g \rightarrow 1^1B_{3u}$ and $1^1A_g \rightarrow 1^1B_{2u}$ transitions are obtained if individually optimized CASSCF wave vectors are replaced by state-averaged CASSCF reference states for the CASPT2 calculations. For comparison, Table III of Ref. 2 reports estimates of 4.22 eV and 5.05 eV for E_1 and E_2 obtained by MRCI calculations including the Davidson size-consistency correction in combination with a double-zeta-polarization level basis set. If predictions of the vertical excitation energy of a certain valence state computed by a variety of available electronic structure methods are considered, the CASPT2 method is well known to locate the transition energy at the low end of this range.

The following maximum occupation numbers have been defined for the harmonic-oscillator basis sets representing the six normal modes: ν_1^{max}=46, ν_2^{max}=6, ν_{6a}^{max}=30, ν_{8a}^{max}=6 and ν_{9a}^{max}=6 and ν_{10a}^{max}=42, resulting in dimensions of 12519360 of the Hamiltonian matrices for both B_{2u} and B_{3u} vibronic symmetries. 18000 Lanczos iterations have been found sufficient to obtain converged spectra in the present application. The diagonalization of one submatrix requires allocation of 1.7 GB of memory and ca. 18h CPU time on a 2.3 GHz AMD Opteron in serial mode.

TABLE I. Experimental[3] (determined from gas-phase electron diffraction data) and theoretical values for the 1^1A_g equilibrium configuration of pyrazine. The geometry has been optimized at the CASPT2 level of theory. Bond distances are in Å, bond angles in degrees.

	experiment	CASPT2
N–C	1.339(2)	1.341
C–C	1.403(4)	1.396
C–H	1.115(4)	1.081
∠C-N-C	115.6(4)	115.25
∠N-C-C	122.2(4)	122.37
∠N-C-H	113.9(10)	116.91

TABLE II. First and second derivatives of the excitation energies of the 1^1B_{3u} and 1^1B_{2u} states of pyrazine with respect to the totally symmetric normal coordinates defined at the 1^1A_g equilibrium geometry (see Table I). The ground and excited state calculations have been performed at the single-state CASPT2 level of theory within D_{2h} symmetry. The unit is eV.

	Q_1	Q_2	Q_{6a}	Q_{8a}	Q_{9a}
$\kappa^{(1)}$	-0.02990	0.02206	-0.08487	-0.09680	0.11659
$\kappa^{(2)}$	-0.16921	0.02082	0.11330	0.02204	0.04116
$\gamma^{(1)}$	0.00026	0.00047	0.00210	-0.00589	-0.00383
$\gamma^{(2)}$	0.00283	0.00001	-0.00606	0.00408	0.00172

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[*] shiozaki@northwestern.edu; Now at Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston 60208, U.S.A.

[†] werner@theochem.uni-stuttgart.de

[‡] woywod@ch.tum.de

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