**Vibronic and Spin–Orbit Coupling Effects in the Absorption Spectra of Pyrazine: A Quantum Chemical Approach**

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*Abstract:* Derivatives of dipole transition moments between spin–orbit coupled multireference configuration interaction wave functions have been used in conjunction with vibrational frequencies from density functional theories to compute vibronic S1←S0 (11B3u←11Ag ) and T1←S0 (13B3u←11Ag ) absorption spectra in Herzberg–Teller approximation. Experimentally known spectra are well reproduced. The calculations reveal unexpectedly small spin–orbit couplings between the 13B3u (3nπ\*) state and nearby optically bright 1B2u (1ππ\*) states, thus explaining the absence of the 1b1g0 1 (ν10a01) fundamental in the vibrational fine-structure of the T1←S0 transition. Adiabatically, two triplet states are found below the S1 state. The out-of-plane distorted T2 minimum results from a pseudo Jahn-Teller interaction between two 3ππ\* states of B1u and B2u symmetry. At the *D2h*-symmetric S0 and S1 minimum geometries, the latter states are located well above S1. The S1 and T2 potentials intersect at geometries far away from the Franck-Condon region. This explains the apparently contradictory results that the linewidth in the higher energy regime above the T1←S0 origin suddenly broadens while no trace of a second triplet state, located energetically below the S1 origin, could be identified in phosphorescence excitation spectra of the ultracold isolated pyrazine molecule.

*Keywords:* density functional theory; multireference configuration interaction; Herzberg–Teller coupling; singlet–triplet transitions; azabenzenes.

RUNNING TITLE: SPIN–VIBRONIC COUPLING IN PYRAZINE

INTRODUCTION

Pyrazine (1, 4-diazabenzene) is a prominent example where it has proven necessary to go beyond the Franck-Condon approximation for understanding the intensity distribution in the S1←S0 absorption spectrum. Its first excited singlet state is of nπ\* type and known to borrow intensity from higher-lying optically bright ππ\* states by vibronic coupling via the ν10a (b1g) and ν5 (b2g) vibrational modes. A comprehensive review of the experimental and theoretical knowledge on its vibronic spectra as of 1988 has been presented by Innes *et al*.1

For the corresponding singlet–triplet absorption, similar vibronic activity might be expected as the vibrational frequencies in the first excited triplet state closely resemble those of S1.2 In contrast to the S1←S0 absorption, the T1←S0 phosphorescence excitation spectrum in a supersonic jet shows no evidence of strong vibronic coupling.Tomer *et al.*3 report that the fundamental ν10a01 and ν501 transitions are absent in the T1←S0 spectrum. Instead, overtones of ν10a  are seen in phosphorescence excitation spectra of neat crystals.1 Another intriguing experimental result concerns the question whether one or two triplet states are located below S1. Hochstrasser and Marzzacco4 observed a sudden increase of bandwidth from 1 cm-1 to 15 cm-1 in the singlet-triplet absorption spectrum of pyrazine crystals at 4.2 K, about 1600 cm-1 above the origin transition. Methylation of pyrazine in 2- and 6-positions lowers this threshold to about 50 cm-1 while tetramethylpyrazine shows only a diffuse spectrum. These results were interpreted as a manifestation of a perturbation on the 3nπ\* state by a 3ππ\* state that is located below the first excited singlet state and has negligible electric dipole oscillator strength.4 Resonance-enhanced multi-photon ionization experiments in supersonic jets point in the same direction. Villa *et al.*5 were unable to induce one-color photoionization of 2-methylpyrazine when the excitation energy was tuned to higher-lying vibronic levels of T1. These authors consider displacements along a vibronically active out-of-plane coordinate due to strong pseudo-Jahn-Teller distortion as a possible cause for poor Franck-Condon factors aggravating the one-color photoionization. However, no trace of a second triplet state, located energetically below the S1 origin, could be found in phosphorescence excitation spectra of the ultracold isolated pyrazine molecule.3 Signals appearing in the T1←S0 absorption spectra in this energy regime at higher temperatures were interpreted as hot bands of the S1←S0 absorption.2,3,6

So far, quantum chemical simulations of the vibronic spectra of pyrazine focussed on the singlet absorption and fluorescence. Woywod *et al.7* employed a vibronic-coupling model Hamiltonian based on the Taylor expansion of diabatic potentials to model the absorption spectrum of the interacting S1–S2 manifold. Besides the S1–S2 coupling mode ν10a, they took three totally symmetric tuning modes (ν1, ν6a, ν9a) into consideration. Berger *et al.8* used a Herzberg-Teller expansion in all vibrational coordinates to model the S0–S1 absorption and fluorescence spectra at 0 and 300 K. Herein, the strongly anharmonic ν10a coupling mode was expanded in terms of harmonic oscillators. Weber and Reimers9 presented an extensive quantum chemical study on the vibrational frequencies in the T1 state but did not address any spin-forbidden T1–S0 transitions. Siebrand and Zgierski10 as well as Fischer2 modelled the interaction between vibronic and spin–orbit coupling in pyrazine, but they had to estimate the magnitudes of the coupling matrix elements or treated them as fitting parameters.

The main focus of the present paper is on the apparent contradictions relating to the interpretation of the measured T1←S0 and S1←S0 spectra of pyrazine. In particular, we want to understand why the T1←S0 spectrum shows significantly less vibronic activity than the S1←S0 spectrum. Further, we will try to clarify the energetic position of the T2 state and its possible role in the spectral broadening of the higher-lying T1←S0 bands. To this end, we carry out extensive quantum chemical calculations on the ground and electronically excited states of pyrazine including both vibronic and spin–orbit coupling effects.

THEORY AND COMPUTATIONAL METHODS

In the framework of the Franck–Condon (FC) approximation,11,12 the transition moment in an intensity calculation of molecular absorption or emission spectra can be written as a simple product of an electronic term and FC factors depending solely on the vibrational degrees of freedom. For strong electronic transitions of polyatomic molecules, *e.g.* spin-allowed ππ\* transitions, this approximation is usually sufficient to describe the intensity distribution of the vibrational fine-structure of a band. The picture changes when it comes to electronic transitions with small oscillator strengths, *e.g.* nπ\* excitations of heteroaromatic molecules, or if highly resolved spectra are to be interpreted. In this case, the transition moment cannot be considered independent of the nuclear motion and the coupling between the vibrational and electronic degrees of freedom, *i.e.,* vibronic coupling has to be taken into account in the modelling. For small triatomic and tetraatomic molecules, sophisticated Hamiltonians have been worked out by Perić and co-workers13,14,15 which include these couplings and are applicable to vibronic transitions involving even large-amplitude motions. In the more general case of polyatomic molecules, the formulation of such model Hamiltonians is too complicated and simpler strategies have to be pursued. One way to proceed is to follow the approach of Herzberg and Teller who formulated a coupling model in which the electric dipole transition moment is expanded about a reference point (typically the equilibrium geometry *Q0*) as a function of the normal mode displacements *Qk*.16

|  |  |
| --- | --- |
|  | (1) |

If the normal mode composition differs strongly between the initial and final states of the transition, it is wise to include Duschinsky effects17 in the Herzberg–Teller (HT) treatment of the vibronic coupling.18 A further complication arises if the initial and final states exhibit different spin multiplicities which is the case, *e.g*., in singlet–triplet transitions. In these cases, an additional coupling term between the spin and spatial electronic angular momenta is required in the Hamiltonian to make the radiative transition allowed.19 Perturbation theories addressing spin–forbidden radiative transitions by sum-over-states expressions are known to be slowly convergent with respect to the number of states included.20 Here, we propose a conceptually simple, though resource-intensive way to include spin–orbit coupling and Herzberg–Teller coupling simultaneously. To this end, spin–orbit-coupled correlated wave functions Ψi and Ψj and the corresponding electric dipole transition moments are generated by a variational multireference spin–orbit configuration interaction (MRSOCI)21 procedure and the first derivative of the transition matrix element with respect to the dimensionless normal coordinate *Qk* is calculated by finite differences

|  |  |
| --- | --- |
|  | (2) |

where *∈k* denotes the unit vector in the direction of the normal mode *Qk* and ε is the step length.

The electronic ground-state geometry of pyrazine was optimized at the level of density functional theory (DFT). For the optimization of excited singlet states, full linear response time-dependent density functional theory (TDDFT) was used while the Tamm-Dancoff approximation (TDA) was employed for triplet calculations.22 Herein, the PBE0 density functional23,24 in combination with a valence triple zeta basis set with polarization functions (TZVP)25 was utilized. All structures were optimized starting with *D2h*-symmetry constraints, while lowering the point-group symmetry if the stationary point turned out to be a saddle point. For an easier comparison with the experimental literature, the *D2h*-symmetric molecule was chosen to lie in the yz plane, with the z axis running through the nitrogen centres. The geometry optimizations and the computation of two-electron integrals in a resolution-of-the-identity (RI) approximation were performed with the Turbomole 7.1 program package26. In the RI step, auxiliary basis sets27 optimized for Møller–Plesset calculations were engaged. Minima were verified by numerical harmonic frequency analysis utilizing the SNF program28. The numerical frequencies were scaled by 0.9944 to account for systematic errors of the PBE0 functional.29

To calculate vertical excitation energies, dipole transition moments and oscillator strengths at DFT or TDDFT optimized geometries, the DFT/MRCI method was used employing the original Hamiltonian developed by Grimme and Waletzke.30,31 Herein, Kohn-Sham molecular orbitals (MOs) in conjunction with the BH-LYP density functional32,33 serve as the one-particle basis. Secular equations for the electronic ground state and 40 excited singlet and triplet states, distributed equally over all irreducible representations, were solved. The DFT/MRCI wave functions were used to calculate spin–orbit coupling matrix elements (SOCMEs) utilizing the spin–orbit coupling kit (SPOCK)34,35 developed in our laboratory. In SPOCK, an effective one-electron spin–orbit mean-field (SOMF) Hamiltonian36 is used which treats the two-electron interactions in a Hartree-Fock like manner. Additionally, the one-centre atomic mean-field integral (AMFI)37 approach is used to reduce the computational cost. Spin–orbit coupled wave functions for the lowest 20 states and their electric dipole transition moments µ in length form were determined using DFT/MRSOCI method21 implemented in SPOCK.

First-order derivatives of the dipole transition moments µ at the ground state geometry were computed numerically. To this end, the minimum structure was distorted by ±0.1 units along the dimensionless normal modes. At each distorted geometry, DFT/MRCI and concomitant DFT/MRSOCI single-point calculations were carried out, followed by a computation of the dipole transition moment and its first derivative according to Eq. (2). A complication arises due to the fact that the phases of the matrix elements are arbitrary. They are determined by the phases of the wave functions Ψi and Ψj and of the MOs from which the determinants are constructed. These phases can change from point to point. Tatchen *et al*.38 used reference matrix elements involving a third, strongly coupling state to fix the phases of the matrix elements relative to the undistorted geometry. In the pyrazine case, dipole transition matrix elements between the ground state (Ag) and the first excited singlet or triplet state (B3u) are needed. For this combination of *gerade* and *ungerade* states, a reference state with two non-vanishing couplings cannot be found. Therefore, we employ a more rigorous approach to fix the phases. At each displaced geometry, the MO phases were set to match the ones of the equilibrium geometry. To accomplish this, we calculated the overlap matrix between both structures. The off-diagonal blocks of the overlap matrix easily show whether MOs changed their phases or switched their ordering. The phases of the DFT/MRCI wave functions were adjusted such that the largest coefficient of each wave function is positive.

Franck–Condon and Herzberg–Teller absorption spectra were obtained by a Fourier transform approach implemented in the VIBES program39,40. In calculating the integrals over the vibrational wave functions of the initial and final states, a Duschinsky transformation17 was applied. Temperature effects were included assuming a Boltzmann population of the vibrational levels in the initial state. Before integration (time interval 5.5 ps, 2×105 grid points), the time correlation function was damped with a Gaussian of 5 cm-1 full width at half maximum.

RESULTS AND DISCUSSION

**Electronic ground and excited states**

Vertical and adiabatic DFT/MRCI excitation energies, computed at DFT/TDDFT converged geometries in *D2h-*symmetry, are listed in Table I. Excited states of *gerade* symmetries have been omitted from this list because they are dark for electric dipole transitions from the ground state in FC approximation and do not lie among the lowest singlet or triplet states. The T1 (13B3u) and S1 (11B3u) states correspond to nπ\* excitations from the highest occupied molecular orbital (HOMO), an in-plane orbital of n/σ type, to the lowest unoccupied molecular orbital (LUMO) of π\* type (FigureI). Their adiabatic energies are close to the experimental band origins.1 This is also true for the optically bright 1ππ\* states, 11B2u and 11B1u, and the second *ungerade* 3nπ\* state, 13Au. Note, however, that the *D2h*-symmetric stationary points of the latter states represent only transition states. While the *D2h-*constrained adiabatic excitation energies of all other states are within ≈ 0.2 eV of the experimental data, we notice an untypical deviation by ≈ 0.7 eV for the corresponding 11Au (HOMO→LUMO+1) state. Because the 11Au←11Ag transition is optically forbidden, the assignment of a broad band at approximately 5.0 eV in a near-threshold electron-energy loss spectrum was based on older MRCI calculations41. This energy regime corresponds roughly to the vertical excitation energy of this transition in our calculations. We also list vertical excitation energies of a few higher-lying bright singlet states which play a key role in the singlet-triplet absorption spectrum with regard to intensity borrowing. The lowest 1ππ\* states have multiconfigurational character: 11B2u and 21B2u (HOMO- 1→LUMO with admixtures of HOMO-2→LUMO+1 and *vice versa*), 11B1u and 21B2u (HOMO-1→LUMO+1 with admixtures of HOMO-2→LUMO and *vice versa*). 41B2u represents a high-lying optically bright mixed nσ\* and Rydberg state (HOMO→LUMO+3) which lends intensity to the triplet absorption.



Figure I. Molecular orbitals at the ground state minimum relevant for spin–orbit coupling.

Table I. DFT/MRCI excitation energies compared with experimental results taken from Fischer2. Vertical excitation energies and oscillator strengths are given at the ground state minimum.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| State | Character | ΔEDFT/MRCI / eV | | | ΔEexp / eV |
|  |  | Vertical | Relaxed(*D2h*) | Adiabatic |  |
| 11Ag |  |  | 0.00 |  | 0.00 |
| 13B3u | n → π\* | 3.56 | 3.46 | 3.46 | 3.33 |
| 11B3u | n → π\* | 4.03 (0.01102) | 3.92 | 3.92 | 3.83 |
| 13B1u | π → π\* | 4.39 | 3.93† | 3.72 (*C1*) | 4.0 |
| 13B2u | π → π\* | 4.34 | 4.17† |  | 4.4 |
| 13Au | n → π\* | 4.89 | 4.18† |  | 4.2 |
| 11Au | n → π\* | 4.97 (0.0) | 4.29† | 3.99 (*C2h*) | 5.0 |
| 11B2u | π→ π\* | 5.09 (0.10819) | 4.82† |  | 4.7 |
| 11B1u | π→ π\* | 6.78 (0.09446) | 6.46† | 5.34 (*C1*) | 6.31 |
| 21B2u | π→ π\* | 7.90 (0.54281) |  |  |  |
| 21B1u | π→ π\* | 7.96 (0.60557) |  |  |  |
| 41B2u | n→ σ\*/Ry | 8.62 (0.35365) |  |  |  |

† saddle point

Using *D2h*-symmetry constraints, only the 1Ag and 3B3u optimizations could be verified as minima. For the first excited singlet state, 11B3u,one imaginary frequency was obtained for a b3g mode. A scan of the energy profile along this mode revealed that the potential energy surface exhibits a shallow double well at the TDDFT level whereas a true minimum is found at the DFT/MRCI level. To obtain an estimate of the force constant of this mode, we used the curvature of the outer branches of the TDDFT scan to fit the harmonic frequency. Herein, data with a distance of at least 3.5 units and at most 4.5 units away from the undistorted geometry were used. This fit yields a harmonic frequency of 1025 cm-1 for the3b3g mode which matches nicely the frequency of 1075 cm-1 in the related 13B3u potential. The geometrical parameters of these minima may be found in Table II.

Table II: Geometrical parameters of ground and first excited singlet and triplet state obtained with TDDFT (TZVP/PBE0).

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| State | CC / Å | CN / Å | CH / Å | ∠ NCC / ° | ∠ CNC / ° | ∠ NCH / ° |
| 1Ag | 1.389 | 1.328 | 1.086 | 122.0 | 115.9 | 117.1 |
| 3B3u | 1.389 | 1.335 | 1.084 | 120.0 | 115.9 | 117.1 |
| 1B3u | 1.385 | 1.339 | 1.083 | 120.4 | 119.1 | 120.0 |
| 1Au (*C2h*) | 1.413 | 1.289/1.362 | 1.089 | 122.0/116.2 | 121.8 | 120.2/122.0 |
| 3B1u (*C1*) | 1.465 | 1.283/1.396 | 1.089/1.082 | 120.4/117.6 | 112.7 | 118.8/118.0 |
| 1B1u (*C1*) | 1.452 | 1.301/1.372 | 1.089/1.085 | 117.4/116.2 | 112.8 | 119.3/117.9 |
|  |  |  |  |  |  |  |
| Experiment25 | 1.403 | 1.339 | 1.115 | 122.2 | 115.6 | 113.9 |

Further optimizations led to minimum structures for 13B1u, 11Au and 11B1u. The molecule retains planarity in the 11Au state, but in-plane movement of both nitrogen atoms in opposite directions lowers the symmetry towards *C2h*. In the case of 13B1u and 11B1u, the symmetry is completely broken. In addition to an asymmetric stretch of the C-N bonds, we observe a twist of the C-C bonds by about 30° on each side (Figure II, left). Its electronic structure points toward a pseudo Jahn–Teller rotation with the B2u state (Figure II, right). Despite the out-of-plane distortion of the nuclear arrangement, the ππ\* electronic character of the state is widely preserved.



Figure II. Top and side view of the T2 minimum structure (left) and molecular orbitals involved in the excitation at the T2 minimum geometry (right).

The question, whether a second triplet state is located below or above the S1 state, has been heavily debated in the literature2,3,4,5. Our DFT/MRCI calculations place the 13B1u state (3ππ\*) state vertically ≈ 0.36 eV above the S1 state in the FC region and ≈ 0.63 eV above the S1 state at the S1 minimum geometry. Geometry optimization in the T2 potential leads to the highly distorted minimum (Figure II, left) with an adiabatic excitation energy ≈0.20 eV below the S1 and ≈0.24 eV above the T1 minimum. The latter value agrees well with the estimated T2-T1 splitting of 1600 cm-1 (≈0.20 eV) deduced by Hochstrasser and Marzzacco4 from the onset of the spectral broadening in their experiments. The presence of an intersection between the S1 and T2 potentials far away from the FC region and the S1 minimum geometry provides a rationale for the conflicting experimental findings that (1) sharp absorption bands can be observed in a narrow energy regime above the origin of the 11B3u←11Ag transition and that (2) there is significant line broadening in the region between the S1 and T1 origins even at cryogenic temperatures3,4 which precludes their assignment as hot bands of the 11B3u←11Ag absorption.

**Vibrational frequencies**

The calculated vibrational frequencies of the 11Ag ground state as well as the 13B3u and 11B3u. excited states are generally in good agreement with the experimentally obtained ones (Table III). An exception, relevant for the discussion of the vibronic spectra in the next section, is the 1b1g (ν10a) frequency in the 11B3u state which is overestimated by 89 cm-1 relative to its experimentally deduced value of 383 cm-1. Berger *et al*.8 have shown that it is necessary to go beyond the harmonic oscillator approximation to describe this vibration appropriately. Most frequencies vary only slightly among the three states. They can nevertheless appear prominently in the FC spectrum if their origins are markedly displaced. In a molecular transition in which the initial and final electronic states retain *D2h* symmetry, this requirement can only be fulfilled by totally symmetric (ag) tuning modes. The modes 1b3u (ν16b), 1b2g (ν4), 1b1g (ν10a) and 3b3g experience large frequency changes going from the ground state to the excited states. Their overtones are expected to be seen in the FC spectra, too. Moreover, the 1b1g (ν10a) and to a lesser extent also the 1b2g (ν4) and 2b2g (ν5) modes are made responsible for strong vibronic coupling in the singlet moiety.2,42 Since the frequency changes are similar in the 13B3u potential, the question arises why their fundamentals are absent or at least very weak in the singlet-triplet absorption.3,4

Table III: Vibrational frequencies of ground state and first excited singlet and triplet states compared to experimental values from Tomer et al.4

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  |  | 1Ag / cm-1 | | 1B3u / cm-1 | | 3B3u / cm-1 | |
| Mode | | Calc. | Exp. | Calc. | Exp. | Calc. | Exp. |
| 1au | 16a | 340 | 342 | 419 | 400 | 440 | 400? |
| 1b3u | 16b | 430 | 416 | 228 | 237 | 261 | 237 |
| 1ag | 6a | 607 | 597 | 618 | 585 | 619 | 620 |
| 1b3g | 6b | 720 | 662 | 693 | 624 | 629 |  |
| 1b2g | 4 | 773 | 705 | 502 | 552 | 405 | 557 |
| 2b3u | 11 | 801 | 791 | 726 | 577 | 729 | 563 |
| 1b1g | 10a | 941 | 918 | 472 | 383 | 285 | 440 |
| 2au | 17a | 969 | 974 | 802 | 743 | 842 |  |
| 2b2g | 5 | 974 | 757 | 805 | 518 | 823 | 522 |
| 1b1u |  | 1033 |  | 617 |  | 619 |  |
| 2ag | 1 | 1052 | 1016 | 1040 | 970 | 1040 | 980 |
| 1b2u |  | 1096 |  | 1083 |  | 1087 |  |
| 2b1u |  | 1173 |  | 1027 |  | 1026 |  |
| 2b2u |  | 1246 |  | 1299 |  | 1318 |  |
| 3ag | 9a | 1257 | 1232 | 1197 | 1104 | 1201 | 1146 |
| 2b3g |  | 1371 |  | 1289 |  | 1304 |  |
| 3b2u |  | 1446 |  | 1370 |  | 1364 |  |
| 3b1u |  | 1520 |  | 1393 |  | 1399 |  |
| 3b3g |  | 1605 |  | 1025\* |  | 1075 |  |
| 4ag | 8a | 1634 | 1579 | 1561 | 1377 | 1579 | 1230 |
| 4b3g |  | 3159 |  | 3164 |  | 3187 |  |
| 4b1u |  | 3160 |  | 3174 |  | 3188 |  |
| 4b2u |  | 3174 |  | 3196 |  | 3211 |  |
| 5ag |  | 3180 |  | 3200 |  | 3214 |  |

**S1 ← S0 absorption spectra**

The FC and HT S1 ← S0 absorption spectra, calculated for 0 K and 293 K, respectively, are shown in Figure III and Figure IV. The dipole transition moment of the 11B3u←11Ag absorption has a value of -0.33395 ea0 in FC approximation which is indicative of a moderately strong electronic transition. As expected for transitions between two *D2h*-symmetric states, only totally symmetric modes, here 1ag (ν6a) and 3ag (ν9), generate high-intensity peaks in the FC spectrum. In addition, overtones of 1b3u (ν16b), 1b1g (ν10a), and 1b2g (ν4) modes are visible. When HT coupling is switched on, additional transitions become symmetry-allowed. The derivatives of µ with respect to the vibronically most active modes are displayed in Table IV. Distortions along the 1b1g (ν10a) normal modes generate the by far largest gradients, explaining the intensity borrowing from the optically bright 11B2u←11Ag and 21B2u←11Ag excitations. The 1b1g0 1 (ν10a01) fundamental and a 1ag0 1 1b1g0 1 (ν6a01 ν10a01) combination transition are clearly visible in Figure IV. Vibronic coupling to 1B1u←11Ag transitions via the 1b2g (ν4) and 2b2g (ν5) modes leads to minor peaks in the HT spectrum. The ag modes are HT active to a lesser extent. Their contributions cause small intensity changes of the FC allowed transitions only. Apart from the slight spectral shifts of the bands engaging the 1b1g (ν10a) mode, the agreement between the simulated 0K spectrum (Figure III) and the supersonic jet spectrum of Tomer *et al.3* is very good, thus lending support to our theoretical approach. When heating up to 293 K, hot bands appear near the 0-0 signal in the simulated spectrum (Figure IV). These hot bands are also present in the vapor spectrum measured by Nakamura6 at 300 K.



Figure III. Franck-Condon and Herzberg-Teller S1 ← S0 absorption spectra at 0 K.



Figure IV. Franck-Condon and Herzberg-Teller S1 ← S0 absorption spectra at 293 K.

Table IV. Dipole transition moment derivatives for the S1 ← S0 transition at the ground state geometry

|  |  |  |  |
| --- | --- | --- | --- |
|  | Dipole transition moment derivatives / ea0 | | |
| Mode k | ∂〈1B3u⏐μx⏐1Ag〉/∂Qk | ∂〈1B3u⏐μy⏐1Ag〉/∂Qk | ∂〈1B3u⏐μz⏐1Ag〉/∂Qk |
| 1ag | 0.01009 | 0.0 | 0.0 |
| 1b2g | 0.0 | 0.0 | 0.04610 |
| 1b1g | 0.0 | 0.24924 | 0.0 |
| 2b2g | 0.0 | 0.0 | 0.01295 |
| 2ag | 0.00504 | 0.0 | 0.0 |
| 3ag | 0.00372 | 0.0 | 0.0 |
| 4ag | 0.02028 | 0.0 | 0.0 |
| 5ag | 0.00869 | 0.0 | 0.0 |

**T1 ← S0 absorption spectra**

When simulating the vibrational fine-structure of spin-forbidden radiative transitions, one must simultaneously account for spin–orbit, electric dipole and vibronic couplings.10,19,43 To this end, we calculated electric dipole transition moments of the multiplicity-mixed DFT/MRSOCI wave functions engaged in the T1←S0 absorption and their derivatives with respect to all normal modes. These data are sufficient for computing the vibronic singlet-triplet spectra, but they do not provide much qualitative insight. A detailed analysis of the direct and indirect contributions to the intensities will be presented after the discussion of the spectrum. The gradients of the dipole transition moments are all close to zero, indicating that vibronic coupling plays a minor role in the lower part of the T1←S0 absorption spectrum. Accordingly, the FC and HT absorption spectra, displayed in Figure V, look basically the same. This finding is in agreement with the notion that all relatively intensive bands in the first 1250 cm-1 of the T1 ← S0 phosphorescence excitation spectrum, recorded by Tomer *et al*. in a supersonic jet, have been assigned to totally symmetric fundamentals, overtones and combinations.3 We find only one noteworthy fundamental transition from a weakly active HT mode in the low energy regime of the spectrum around 400 cm-1 which we assign to 1b2g01 (ν401). The overtone of that transition gives rise to a more intensive signal around 800 cm-1 for which the assignment by Tomer *et al*.3 was uncertain. The peak at 880 cm-1 in the experimental spectrum is attributed to an overtone of the 1au (ν16a) mode. Consequently, the weak signal at 1114 cm-1 must have a different origin than the assignment (ν402) proposed by Tomer *et al*. We find a combination band 1b3u021b1g0 2 (ν16b02 ν10a02) in this energy regime. Most details of the measured phosphorescence excitation spectrum are well reproduced by our simulation, except for a signal at 570 cm-1 whicharises from the 1b1g0 2 (ν10a02) overtone and which is not observed in that experiment. At the same time, we are missing intensity in the 1ag01 (ν6a01) signal at 620 cm-1. While the frequency of the 1b1g (ν10a) mode was overestimated in the 11B3u state, it appears to be underestimated in the 13B3u potential by our calculations. If placed at slightly higher energy, its first overtone would overlay with the 1ag01 transition and recover the missing intensity of that signal. In addition, the second overtone 1b1g0 4 (ν10a04) would be shifted to about 1200 cm-1 and add to the signal strength of the 3ag01 (ν9a01) fundamental.



Figure V. Franck-Condon and Herzberg-Teller T1 ← S0 SOCI absorption spectrum at 0 K.

The leading terms of the DFT/MRSOCI wave functions and their projections onto the unperturbed DFT/MRCI states are shown in Table V. Under the influence of spin–orbit coupling, the 13B3u state splits into three sublevels with an energy separation of less than 0.1 cm-1. Their individual radiative singlet-triplet transitions are therefore spectrally not resolved.

Table V. Spin–orbit coupled states calculated by DFT/MRSOCI at the S0 minimum geometry.

|  |  |  |
| --- | --- | --- |
| State | Projection onto DFT/MRCI states | |
|  | Largest triplet contributions | Largest singlet contributions |
| 1 | 13B1g((ms = 1) - (ms = -1)) (8.0 × 10-4 *i*) | 11Ag (**0.99999**) |
| 2 | 13B3u(ms = 0) (**-0.99999 *i***) | 21Au (-5.7 × 10-4) |
| 3 | 13B3u((ms = 1) + (ms = -1)) **(-0.69301 + 0.14049** *i*) | 11B2u ( 1.3 × 10-4 - 0.3 × 10-4 *i*)  41B2u (-1.3 × 10-4 + 0.3 × 10-4*i*) |
| 4 | 13B3u((ms = 1) - (ms = -1)) (**0.00384 + 0.70710 *i***) | 11B1u ( 2.7 × 10-4)  21B1u (-4.0 × 10-4) |
| 5 | 13B1u((ms = 1) - (ms = -1)) (2.9 × 10-3 *i*)  23B1u((ms = 1) - (ms = -1)) (1.4 × 10-3 *i*)  13B2u((ms = 1) + (ms = -1)) (-7.8 × 10-4) | 11B3u **(-0.99999**) |

Setting aside triplet-triplet transitions, there are two symmetry-allowed pathways which do not involve vibronic activity. They are characterized by intensity borrowing from intermediate B1u and B2u singlet states. The third pathway via 1Au states is electric dipole forbidden in *D2h* symmetry. We will therefore have a closer look at matrix elements of the type 〈13B3u⏐HSO⏐1B1u〉 〈1B1u⏐er⏐11Ag〉 and 〈13B3u⏐HSO⏐1B2u〉 〈1B2u⏐er⏐11Ag〉.

The lowest excited SOCI state consists mostly of the ms = 0 component of the 13B3u state. It exhibits Au combined spatial and spin symmetry and is therefore not visible in the FC spectrum. The second excited SOCI state is dominated by the positive linear combination of the ms = 1 and ms = -1 spin components of the 13B3u state. With the present choice of coordinate axes, this transition is y-polarized and borrows its intensity mainly from 1B2u states. Although the interacting states have different orbital character and the coupling is allowed according to the El-Sayed rules44, the SOCMEs between the 3nπ state and the two lowest 1ππ\* states of B2u symmetry are surprisingly small (〈13B3u⏐HSO⏐11B2u〉 = -1.63 cm-1, 〈13B3u⏐HSO⏐21B2u〉 = 0.36 cm-1). To rationalize this result, one must remember that the spin–orbit Hamiltonian is short-ranged and dominated by effective one-electron terms. The leading configurations of the 13B3u and 11B2u wave functions differ by a HOMO-1→HOMO single excitation and could hence be connected by a one-electron operator. Closer inspection of the involved orbitals (Figure I) reveals, however, that the HOMO-1 has a nodal plane running through the nitrogen atoms where the HOMO exhibits the largest amplitudes. The main configuration of the second singlet state in B2u symmetry is doubly excited with respect to the dominant 13B3u configuration. Their coupling would require two-electron terms of the spin–orbit Hamiltonian which are much smaller than the effective one-electron terms. A medium-sized SOCME is found for the higher-lying 41B2u state of 1nσ\* type (〈13B3u⏐HSO⏐41B2u〉 = 5.28 cm-1) which is connected to the 13B3u state by a LUMO→LUMO+3 excitation in the orbital picture. The coupling is caused mostly by one-centre integrals between basis functions at carbon atoms which are smaller than the corresponding integrals at nitrogen atoms due to the reduced nuclear charge. The moderate spin–orbit interaction between the 13B3u state and the 1B2u states is not the only reason why the transition to this triplet substate is very weak. The relative phases of the 11B2u and 41B2u coefficients in the second excited SOCI wave function are such that their dipole transition moments (Table VI) nearly cancel. The T1 ← S0 absorption and the corresponding phosphorescence derive their intensities nearly exclusively from z-polarized transitions to the third triplet sublevel. Its SOCI wave function is dominated by the negative linear combination of the ms = 1 and ms = -1 spin components of the 3B3u state. This substate mainly borrows intensity from the bright 11B1u and 21B1u states. Their spin–orbit interactions with the 13B3u state are stronger than for the B2u-symmetric ππ\* states (〈13B3u⏐HSO⏐11B1u〉 = 6.89 cm-1, 〈13B3u⏐HSO⏐21B1u〉 = -13.97 cm-1). The different magnitudes of the SOCMEs can be rationalized by investigating the MOs involved in the couplings. The two lowest 1B1u states are multiconfigurational states with major contributions from HOMO-1→LUMO+1 and HOMO-2→LUMO excitations. While the former represents a double excitation with respect to the leading HOMO→LUMO term of the 13B3u state and does not couple via an effective one-electron operator, the latter is connected to 13B3u by a single excitation from HOMO-2 to HOMO. Their spin–orbit integral is quite large as both MOs exhibit substantial amplitudes at the nitrogen atoms. The intensity contributions from the 11B1u and 21B1u states partially cancel as well, but the remainder is larger owing to the larger weighting coefficient in the SOCI expansion and the substantial dipole transition moment of the 21B1u←11Ag transition.

Table VI. DFT/MRCI dipole transition moments with respect to the electronic ground state

|  |  |
| --- | --- |
| State | Dipole transition moment [ea0] |
| 11B2u | 0.9316 (y) |
| 41B2u | 1.1174 (y) |
| 11B1u | 0.7543 (z) |
| 21B1u | 1.7919 (z) |

The intensity of the 1b1g (ν10a) fundamental in the T1 ← S0 spectrum is governed by matrix elements of the form2,3,10 〈13B3u⏐HSO⏐11B2u〉 〈11B2u⏐Hvib (b1g)⏐11B3u〉 〈11B3u⏐er⏐11Ag〉 and 〈13B3u⏐Hvib (b1g)⏐13B2u〉 〈13B2u⏐HSO⏐11B3u〉 〈11B3u⏐er⏐11Ag〉. The first spin–vibronic pathway via the 1b1g (ν10a) mode would engage the same small SOCME as the one involved in the direct SOC mechanism of the second triplet substate. The second spin–vibronic pathway involves the S1 (11B3u) state and the B2u symmetric triplet state. The contributions of the 13B2u substates to the SOCI wave function of the S1 state are somewhat larger than those of the 11B2u state in the T1 wave function (Table V). Siebrand and Zgierski argued that the vibronic intensities induced via the two pathways might cancel out due to interference.10 We cannot exclude this possibility, but we consider the electronic structures of the involved states and their weak SOC the main reason for the missing vibronic activity of the 1b1g (ν10a) mode in the T1 ← S0 spectrum. In analogy, we expect matrix elements of the form 〈13B3u⏐HSO⏐11B1u〉 〈11B1u⏐Hvib (b2g)⏐11B3u〉 〈11B3u⏐er⏐11Ag〉 and 〈13B3u⏐Hvib (b2g)⏐13B1u〉 〈13B1u⏐HSO⏐11B3u〉 〈11B3u⏐er⏐11Ag〉 to govern the intensity of the vibronic coupling via the 1b2g (ν4) and 2b2g (ν5) modes. The SOCMEs are much larger in this case. We expect the vibronic coupling terms 〈11B1u⏐Hvib (b2g)⏐11B3u〉 to be limiting factors in these pathways because the frequency shifts of the b2g modes are not very pronounced. Indeed, we see traces of HT activity of the 1b2g (ν4) mode in the singlet-triplet absorption spectrum (Figure V) around 400 cm-1.

We did not investigate the vibronic fine-structure in the higher energy regime of the T1 ← S0 absorption. Our results suggest, however, that nonadiabatic coupling between T1 and the highly distorted T2 (13B1u) state, whose minima are located energetically below the S1 minimum, will lead to substantial broadening of the signals. Tomer *et al*.3 did not find any evidence for a 13B1u state in the phosphorescence excitation spectrum of the isolated pyrazine molecule. We explain this fact by the double-well shape of the T2 potential with a saddle point at *D2h*-symmetric structures and nearly vanishing 0-0 vibrational overlap between the 13B1u and 11Ag states. This interpretation is also compatible with the lack of intensity in the one-color photoionization spectrum of 2-methylpyrazine which was ascribed to be due too poor Franck-Condon factors caused by pseudo-Jahn-Teller out-of-plane distortions.5

CONCLUSION

In the present work, we have studied the spectral properties of pyrazine by means of high-level quantum chemical methods. In addition to the *D2h*-symmetric T1 and S1 (B3u, nπ\*) minima, we find an out-of-plane distorted T2 (ππ\*) minimum with twisted C-C bonds and unequal C-N bond lengths which is located adiabatically below the S1 minimum. Its electronic structure is reminiscent of a mixture between two 3ππ\* wave functions of B1u and B2u symmetry. At the *D2h*-symmetric S0 and S1 minimum geometries, the 13B1u and 13B2u states are located well above the S1 state. The 3ππ\* states can interact vibronically with T1 and via spin–orbit coupling with S1. Among the spin–orbit interactions, the couplings between the B3u and B1u states prevail while the couplings between the B3u and B2u states are surprisingly small in light of their respective nπ\* and ππ\* orbital characters. Geometry relaxation in the T2 potential leads to an intersection with the S1 potential energy surface at geometries far away from the Franck-Condon region. We have not quantitatively determined the energetic location of the conical intersection, but the presence of an energy barrier for the intersystem crossing from S1 to T2 qualitatively explains the apparently contradictory experimental observations that sharp lines can be seen in the S1←S0 absorption spectrum above the origin, no trace of a second triplet state could be identified in the phosphorescence excitation spectra of the ultracold isolated pyrazine molecule3 whereas the linewidth in the higher energy regime above the T1←S0 origin suddenly broadens4.

Dipole transition moments between spin–orbit coupled multireference configuration interaction wave functions and their derivatives with respect to all normal coordinates have been used in conjunction with vibrational frequencies from density functional theories to model the vibronic S1←S0 and T1←S0 absorption spectra in Franck–Condon and Herzberg–Teller approximation. The results of our study confirm that vibronic coupling plays an important role in the S1 ← S0 absorption spectrum where the most prominent coupling modes are 1b1g (ν10a) and 1b2g (ν4). The low Herzberg-Teller activity of the 1b1g (ν10a) mode in the T1 ← S0 absorption and phosphorescence excitation spectra was traced back to the unexpectedly small 〈13B3u⏐HSO⏐11B2u〉 and 〈13B3u⏐HSO⏐11B2u〉 matrix elements. The T1 ← S0 absorption and the corresponding phosphorescence derive their intensities nearly exclusively from z-polarized transitions to the third triplet sublevel mainly represented by the negative linear combination of the ms = 1 and ms = -1 spin components of the 3B3u state. The intensity of the spin-forbidden transition is borrowed from the optically bright 11B1u and 21B1u states by a direct spin–orbit mechanism without the necessity to invoke spin–vibronic coupling. The good agreement between our simulated spectra and the experimentally observed ones establishes confidence in the applied quantum methods and the procedures for computing vibronic spectra under the influence of spin–orbit coupling.

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