**Communication: Simulation of the single-vibronic-level emission spectrum of HPS**

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**Abstract**: We have computed the potential energy surfaces of the $\tilde{X}$1A' and $\tilde{A}$1A" states of HPS using the explicitly correlated multi-reference configuration interaction (MRCI-F12) method, and Franck-Condon factors between the two states, which include anharmonicity and Duschinsky rotation, with the aim of testing the assignment of the recently reported single-vibronic-level (SVL) emission spectrum of HPS [Grimminger *et al*, J. Chem. Phys. **139,** 174306 (2013)].

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**Introduction**: Very recently, Grimminger *et al* have reported the $\tilde{A}$1A" - $\tilde{X}$1A' laser induced fluorescence (LIF) and single-vibronic-level (SVL) emission spectra of HPS and DPS.[[1]](#endnote-1) In order to assist spectral assignments, density functional theory (DFT) and *ab initio* calculations were carried out.1 In addition, anharmonic Franck-Condon factors (FCFs) between the two states involved were computed with a “quick and dirty” approach (their quotes; see Ref. 1), employing computed coupled-cluster single and double plus perturbative triples {CCSD(T)} and complete active space self-consistent field multi-reference configuration interaction (including the Davidson correction) (CASSCF/MRCI) potential energy functions (PEFs) for the two electronic states, respectively, using the augmented correlation consistent polarized valence quadruple-zeta {aug-cc-pV(Q+d)Z} basis set. However, although computed FCFs of the $\tilde{A}$1A" ← $\tilde{X}$1A'(0,0,0) excitation of HPS and DPS were published in Ref. 1, a direct comparison between the computed FCFs and experimental LIF spectra of HPS and DPS could not be made, because the observed LIF spectra were not corrected for laser power. Nevertheless, Ref. 1 has reported the 304 SVL emission spectrum of HPS, though not the corresponding computed anharmonic FCFs. In this connection, in the present study, we have carried out FCF calculations, in order to simulate the vibrational structure of the 304 SVL emission spectrum of HPS, with the aim of testing the assignments proposed in Ref. 1. We have used our *ab initio*/FCF method[[2]](#endnote-2),[[3]](#endnote-3),[[4]](#endnote-4) successfully to provide “fingerprint” type assignments of SVL emission spectra of numerous triatomic molecules,[[5]](#endnote-5),[[6]](#endnote-6),[[7]](#endnote-7),[[8]](#endnote-8),[[9]](#endnote-9),[[10]](#endnote-10),[[11]](#endnote-11),[[12]](#endnote-12) including HPO/DPO, [[13]](#endnote-13) which are valence iso-electronic with HPS/DPS. It should be noted that, CCSD(T) and explicitly correlated CCSD(T)-F12 calculations on HPS, its cation and anion, in their ground electronic states, were also published recently together with their CCSD(T)/aug-cc-pV5Z PEFs and anharmonic vibrational energies.[[14]](#endnote-14)

**Computational details**: The explicitly correlated CASSCF/MRCI-F12 (including Davidson corrections)[[15]](#endnote-15),[[16]](#endnote-16) method, as implemented in MOLPRO,[[17]](#endnote-17) was employed, because the $\tilde{A}$1A" state of HPS is an open-shell singlet state, which requires a MR method. In addition, explicitly correlated methods are known to achieve a dramatic improvement of basis set convergence of correlation energies when compared with conventional correlation methods.[[18]](#endnote-18),[[19]](#endnote-19) The cc-pVQZ-F12[[20]](#endnote-20) (or VQZ-F12) and cc-pCVQZ-F12[[21]](#endnote-21) (or CVQZ-F12) atomic orbital basis sets, specifically designed for F12 methods, were used in geometry optimization, together with the corresponding density fitting[[22]](#endnote-22),[[23]](#endnote-23) and resolution of the identity[[24]](#endnote-24) basis sets (see MOLPRO online manual[[25]](#endnote-25)). With the VQZ-F12 basis sets, a full valence active space was employed in CASSCF and subsequent MRCI-F12 calculations. With the CVQZ-F12 basis sets for P and S, a full valence active space was used in CASSCF calculations, but the 2s22p6 core electrons of both P and S were correlated explicitly in subsequent MRCI-F12 calculations. Also, with the VQZ-F12 basis set, the default value of 1.0 was used for the geminal Slater exponent {β, in the nonlinear correlation factor, (r12) = -(1/β)exp(-βr12)} in the MRCI-F12 calculation, while with the CVQZ-F12 basis set, β was set to 1.5. These choices of the F12 basis sets and corresponding β values follow recommendations from a recent investigation on basis sets and core-valence effects with explicitly correlated methods.[[26]](#endnote-26) In addition, 409 and 380 computed CASSCF/MRCI-F12/CVQZ-F12 energies for the $\tilde{X}$1A' and $\tilde{A}$1A" states of HPS, in the ranges of {1.0 ≤ r(PH) ≤ 2.43 Ǻ, 50 ≤ θ(HPS) ≤ 160º, 1.4 ≤ r(PS) ≤ 2.9 Ǻ} and {1.1 ≤ r(PH) ≤ 2.5 Ǻ, 40 ≤ θ(HPS) ≤ 145º, 1.7 ≤ r(PS) ≤ 2.75 Ǻ } respectively, were fitted to potential energy functions (PEFs) of a polynomial form (see Ref.s 8 and 13 for details). Employing these PEFs and the rovibronic Hamiltonian of Watson[[27]](#endnote-27) for a non-linear molecule, anharmonic vibrational wavefunctions (expressed as linear combinations of harmonic oscillator functions) and their corresponding energies were computed. FCFs including anharmonicity and Duschinsky rotations were then calculated as previously.8,9 Various harmonic oscillator basis sets have been used to ensure that basis size effects on computed anharmonic vibrational energies and FCFs are negligibly small. Vibrational components in the $\tilde{A}$1A"- $\tilde{X}$1A' absorption and SVL emission spectra of HPS/DPS were simulated employing computed anharmonic FCFs and frequency factors of 1 and 4, respectively, with Gaussian line shapes and a full-width-at-half-maximum of 10 cm-1.8,9

**Results and discussion**: Computed geometrical parameters and relative electronic energies are given in supplementary material (Table S1). We have also optimized the geometry of the $\tilde{X}$1A' state of HPS at the UCCSD(T)-F12/VQZ-F12 level (Table S1). It is pleasing that the optimized geometrical parameters obtained at the UCCSD(T)-F12 and the MRCI-F12 levels with the VQZ-F12 basis set agree very well (differences of ≤0.003 Ǻ and ≤0.2º). In fact, generally, all computed geometrical parameters shown in Table S1, obtained with default frozen cores for P and S agree very well for both states of HPS. When core electrons of P and S are correlated explicitly, computed re(PH) and re(PS) values decrease, while computed θe(HPS) values increase, for both states of HPS, when compared with the corresponding values obtained with frozen cores. A similar trend is also observed from previous CCSD(T) calculations (*e.g.* with the AV(Q+d)Z1 and cc-pwCVQZ[[28]](#endnote-28) basis sets; Table S1) for the $\tilde{X}$1A' state. Summing up, all computed geometrical parameters are very consistent, particularly for the computed θe values for both states, which have overall spreads of ≤0.6º. The experimental r0 and semi-experimental re geometrical parameters of the $\tilde{X}$1A' state of HPS have been derived in a microwave study.27 Comparing the semi-experimental re values with corresponding computed values (Table S1), the agreement in θe is very good (within 0.4º). Regarding re(PS), the semi-experimental value agrees very well (within 0.0023 Ǻ) with our MRCI-F12/CVQZ-F12 value. However, for re(PH), the semi-experimental value agrees better with the MRCI-F12/VQZ-F12 value (almost identical) than with the MRCI-F12/CVQZ-F12 value (within 0.011 Ǻ). Also, it agrees very well with the CCSD(T)/cc-pwCVQZ value28 (within 0.002 Ǻ).

Regarding Te/T0 values, only computed values obtained at the highest levels of theory are shown in Table S1 (for lower level values, see Ref. 1). It should be noted that the experimental T0 value in Ref. 1 was not obtained by direct measurement. It was derived from vibrational analysis, as the 000 band was not observed in the LIF spectrum of HPS.1 Comparing computed and experimental T0 values, computed values are generally larger than the experimental value, and improvements in the levels of calculation (*e.g.* including core correlation and/or using an explicitly correlated method, which improves basis size convergence) lead to larger discrepancies between theory and experiment. A similar observation was noted in Ref. 1. At the currently highest level, MRCI-F12/CVQZ-F12, the computed T0 value of 12739 cm-1 is 1448 cm-1 (~0.19 eV) larger than the derived experimental value of 11291 cm-1.

 Computed harmonic (ω) and fundamental (ν) vibrational frequencies of all three vibrational modes in the two states of HPS/DPS obtained by different methods are given in Table 1. It can be seen that computed ω values have spreads as large as 44 cm-1 {*e.g.* with ω(PH) of the $\tilde{X}$1A' state of HPS}. Regarding computed ν values, the RCCSD(T)/AV5Z PEF ν(PH) value of 2263.9 cm-1 of the $\tilde{X}$1A' state of HPS from Ref. 14 is most likely a mistake (see footnote b of Table 1). At the same time, the derived ωi0(PH) value of the $\tilde{X}$1A' state of HPS from Ref. 1 is probably not reliable (see footnote d of Table 1). Nevertheless, the agreement between computed MRCI-F12/CVQZ-F12 and available observed ν values of both states of HPS/DPS is reasonably good (within 17 cm-1).

 The simulated $\tilde{A}$1A" ← $\tilde{X}$1A' absorption spectra of HPS and DPS employing the computed MRCI-F12/CVQZ-F12 geometries for the two states involved are given in supplementary material (Figure S1; the HPS spectrum is also in the lower panel of Figure 2). The simulated vibrational structures are essentially identical to the bar diagrams of the computed FCF values reported in Ref. 1, supporting the reliability of the “brute force” (“quick and dirty”) numerical integration method used therein. The good agreement also indicates the similar quality of the two sets of PEFs used.

The simulated 304 SVL {$\tilde{A}$1A"(0,0,4) → $\tilde{X}$1A'} emission spectra of HPS, obtained employing the MRCI-F12/CVQZ-F12 geometries (middle trace) and also the geometries (bottom trace) derived from an iterative Franck-Condon analysis (IFCA; see Ref.s 8 and 13), are shown in Figure 1, together with the experimental spectrum (top trace) from Ref. 1. In the IFCA procedure, the semi-experimental re geometry of the $\tilde{X}$1A' state of HPS28 was used, while the geometrical parameters of the $\tilde{A}$1A" state were varied from the MRCI-F12/CVQZ-F12 geometry until a best match between the simulated and experimental spectra was obtained (vibronic components and relative intensities). Since the published experimental spectrum covers only up to the 1800 cm-1 region (displacement energy from the excitation line), comparison between simulated and experimental spectra can only be made within this region (up to the 22 component; ν1 and ν3 are the HP and PS stretching modes, while ν2 is the bending mode). Comparing the experimental spectrum and the simulated spectrum obtained using the MRCI-F12 geometries (Figure 1, top and middle traces), it can be seen that it is mainly the relative intensity of the $\tilde{A}$1A"(0,0,4) → $\tilde{X}$1A'(0,0,2) vibrational component (32 in Figure 1) which needs adjustment in the IFCA procedure. In order to increase the relative intensity of the simulated 32 component, the PS bond length has to be increased significantly. {Different geometry changes upon excitation (Δre) obtained by different methods are given in Table S1.} Comparing the two simulated spectra obtained using two different sets of geometries (Figure 1, middle and bottom traces), the simulated vibrational structures in the low displacement energy region (<1800 cm-1) are actually quite similar. They differ more at higher displacement energy, specifically in the relative intensities of the 33 and 34 components, though the experimental spectrum1 (top trace of Figure 1) does not cover this energy region.

We have also simulated the absorption spectrum of HPS employing the IFCA geometries of the two states. This simulated band (Figure 2 top trace) extends to very large displacement energies {22000 cm-1 *c.f.* ~15000 cm-1 with the simulated spectrum using the MRCI-F12 geometries (Figure 2 bottom trace)}, with the band maximum at the 307 component (*c.f.* the 302 component with the MRCI-F12 geometries). The 000 component is very weak and will be difficult to be observed experimentally. This appears to be in line with the fact that of the 000 component is not observed in the experimental LIF spectrum.

**Concluding remarks**: We have computed explicitly correlated MRCI-F12 PEFs, which include core correlation, for the $\tilde{X}$1A' and $\tilde{A}$1A" states of HPS, and anharmonic FCFs between the two states. Employing computed FCFs, the 304 and also other 30n SVL emission spectra of HPS were simulated (see Figure S2 in Supplementary material) and compared with the experimental 304 SVL emission spectra. The computed 304 SVL emission spectrum gives the best agreement with the experimental spectrum (Figure 2 of Ref. 1). It is concluded that our spectral simulation supports the assignments of the molecular carrier, the electronic states involved and the vibrational structure of the experimental SVL emission spectrum proposed in Ref. 1. In this connection, we have answered the first of the three unanswered questions raised in the Conclusions of Ref. 1 on the exact assignment of PS stretching quanta in the LIF spectra. However, the remaining two questions on the exact position of the 000 band and the geometry of the excited state remain open. Regarding the 000 position, the rather large discrepancy of 0.19 eV between the computed MRCI-F12/CVQZ-F12 value and the derived experimental value is disappointing. Further experimental and theoretical investigations are required to determine the exact position of the 000 band of HPS and to resolve the discrepancy between theory and experiment on T0. Regarding the geometry of the excited state, our IFCA geometry has a re(PS) value, which is larger than all high level computed values by ~0.1 Ǻ (Table S1), and the IFCA geometries give a simulated absorption spectrum, which is very different from that obtained with the computed MRCI-F12/CVQZ-F12 geometries. It should be noted that the IFCA geometrical parameters were derived based on the published experimental 304 SVL emission spectrum, especially the relative intensity of the relatively weak 32 component. Clearly, there are some experimental limitations: the rather narrow spectral range available in the experimental spectrum, as mentioned, and also some impurity bands and/or overlapping rotational structures, as shown in the experimental LIF spectrum of Ref. 1 (Figure 1 therein), which may have affected the observed SVL emission spectrum. Further spectroscopic and computational investigations will be required to establish the $\tilde{A}$1A"←$\tilde{X}$1A' band origin and the geometry of the excited state. Nevertheless, the reasonably good agreement between the overall vibrational envelopes of the simulated and experimental SVL emission spectra indicates that the experimental spectrum arises from the 304 excitation.

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Table 1. Computed and experimental vibrational frequencies (ωe [ν] values in cm-1) of the $\tilde{X}$1A' and $\tilde{A}$1A" states of HPS and DPS.

|  |  |  |
| --- | --- | --- |
| $\tilde{X}$1A' | HPS | DHS |
| HP | bend  | PS | DP | bend | PS  |
| MRCI-F12/CVQZ-F12 PEFa  | 2298 | 931 | 695 | 1652 | 676 | 695 |
| (as above) ν | [2190] | [911] | [688] | [1594] | [666] | [688] |
| CCSD(T)/AV(Q+d)Z PEF1  | 2274  | 903 | 684 | 1634 | 656 | 684 |
| (as above ; variationally) ν  | [2171] | [887] | [678] | [1582] | [647] | [678.0] |
| MRCI/AV(5+d)Z1  | 2254  | 911 | 682 |  |  |  |
| RCCSD(T)/AV5Z PEF14 | 2273  | 909 | 686 |  |  |  |
| (as above) ν | [2263.9] b | [894.1] | [655.9] |  |  |  |
| CCSD(T)-F12/VQZ-F1214 | 2276  | 906 | 689 |  |  |  |
| SVL emission1 (ωi0 valuesc) | 2178(2)d | 900.5(10) | 683.3(7) |  |  |  |
| SVL emission1 ν | [2177.6] | [894.5] | [682.3]e | - | [651.7] | [682.4] |
| $\tilde{A}$1A" |  |  |  |  |  |  |
| MRCI-F12/CVQZ-F12 PEFa  | 2320 | 707 | 515 | 1666 | 511 | 515 |
| (as above) ν | [2195] | [683] | [511] | [1601] | [499] | [511] |
| MRCI/AV(Q+d)Z PEF1 | 2287  | 694 | 505 | 1642 | 497 | 510 |
| (as above ; variationally) ν  | [2168] | [674] | [500] | [1582] | [490] | [501] |
| LIF1 (ωi0 valuesc) | - | 679(2) | 517.3(10) |  |  |  |
| LIF1 ν | - | [675]f | [515.3] |  |  | [508]g |

a Present study. b This is most likely a mistake, as *x*11 given in Ref. 14 has a value of -64.94 cm-1. c The ωi0 values were derived using equation 2 in Ref. 1. d Note that no *x*11 value is available, as only the 11 component was observed. e Analysis of hot bands in the LIF spectrum gave an energy of 678.1(9) cm-1 for the 31 level. f The 201 LIF band is weak; see Ref. 1. g Separation between the 301 and 302 components.

**Figure Captions**

Figure 1. Simulated 304 SVL emission spectra of HPS employing MRCI-F12/CVQZ-F12 (middle trace) and IFCA geometries (bottom trace; see text) for the $\tilde{X}$1A' and $\tilde{A}$1A" states of HPS, together with the corresponding experimental spectrum (top trace) from Ref. 1.

Figure 2: Simulated absorption spectra of HPS employing MRCI-F12/CVQZ-F12 (bottom trace, as top trace of Figure 1) and IFCA geometries (top trace; see text) at 300 K.

Figure 1. (Mok *et al*)



Figure 2: (Mok *et al*)

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**Supplementary Material**

Table S1. Computed and experimentally derived geometrical parameters (re values, except otherwise stated) of, and excitation energies (Te values, except otherwise stated) between, the $\tilde{X}$1A' and $\tilde{A}$1A" states of HPS.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| $\tilde{X}$1A' | HP/Å  | PS/Å | HPS/deg. | Te/cm-1 |
| UCCSD(T)-F12b/VQZ-F12a | 1.4339  | 1.9332 | 101.84 |  |
| MRCI-F12/VQZ-F12a | 1.4321 | 1.9361 | 101.98 |  |
| MRCI-F12/CVQZ-F12a | 1.4210 | 1.9264 | 102.16 |  |
| MRCI-F12/CVQZ-F12 PEFa | 1.4225 | 1.9256 | 102.13 |  |
| MRCI/AV(5+d)Z1 | 1.4315 | 1.9371 | 102.09 |  |
| CCSD(T)/AV(Q+d)Z PEF1 | 1.4334 | 1.9373 | 101.77 |  |
| CCSD(T)/AV(6+d)Z14 | 1.4335 | 1.9333 | 101.8 |  |
| CCSD(T)/AV5Z PEF14 | 1.4335 | 1.9347 | 102.1 |  |
| UCCSD(T)-F12b/VQZ-F1214 | 1.4335 | 1.9331 | 101.8 |  |
| CCSD(T)/cc-pwCVQZ28 | 1.4303  | 1.9293 | 101.84 |  |
| MW r028 | 1.444(5) | 1.931(1) | 101.6(5) |  |
| MW (semi-experimental re)28 | 1.4321(2) | 1.9287(1) | 101.78(1) |  |
| $\tilde{A}$1A" |  |  |  |  |
| MRCI-F12/VQZ-F12a | 1.4263 | 2.0568 | 91.89 | 12296 |
| (as above) Δreb | -0.0058 | +0.1207 | -10.09 |  |
| MRCI-F12/CVQZ-F12a | 1.4129 | 2.0512 | 92.34 | 12939 |
| (as above) Δreb and T0c  | -0.0081 | +0.1238 | -9.82 | 12739 |
| (as above) T0c DPS |  |  |  | 12770 |
| MRCI-F12/CVQZ-F12 PEFa | 1.4227 | 2.0475 | 91.98 | 12578 |
| (as above) Δreb and T0c | 0.0003 | +0.1219 | -10.14 | 12378 |
| (as above) T0c DPS |  |  |  | 12409 |
| MRCI/AV(Q+d)Z PEF1 | 1.4290 | 2.0635 | 91.74 |  |
| {CCSD(T) & MRCI PEF’s}1 Δreb  | -0.0004 | +0.1262 | -10.03 |  |
| MRCI/AV(5+d)Z1  | 1.4290 | 2.0595 | 92.01 | 12060 |
| (as above)1 T0c |  |  |  | 11880 |
| IFCA geometryd  | 1.424  | 2.155  | 91.5 |  |
| IFCAf Δreb | -0.0081 | +0.2263 | -10.28 |  |
| LIF T0 (estimated)1 |  |  |  | 11291 |

a Present work; see text. b Geometry changes upon excitation. c T0 = Te + Δ(ZPE), with computed ν’s for Δ(ZPE). d The re geometry of the $\tilde{X}$1A' state was fixed to the semi-experimental geometry,28 while the IFCA procedure was employed to obtain the re geometry of the $\tilde{A}$1A" state (see text).

**Figure captions in supplementary material**

Figure S1. Simulated absorption spectra of HPS (top) and DPS (bottom) from the $\tilde{X}$1A' state to the $\tilde{A}$1A" state employing MRCI-F12/cc-pCVQZ PEFs and geometries at 300 K.

Figure S2. Computed relative intensities (in arbitrary units; bar diagrams) of the 30n (n = 0, 1, 2, 3, 4, 5 or 6) SVL emission spectra of HPS obtained using MRCI-F12/CVQZ geometries (Note that comparisons with the experimental 304 SVL emission spectrum of Ref. 1 show clearly that the experimental spectrum cannot be due to the 300, 301, 302 or 303 SVL emission. While the experimental spectrum may be considered to match with the computed relative intensities of the 304 or 305 SVL emissions, if the experimental spectrum is assigned to the 305 SVL emission, the extrapolated T0 position will be considerably smaller than the computed values. Consequently, the experimental SVL emission spectrum is assigned to be arisen from the 304, rather than the 305, excitation.)

Figure S1. (Mok *et al.*)

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Figure S2. (Mok *et al.*)



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