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THE JOURNAL OF CHEMICAL PHYSICS **135**, 074302 (2011)

High-level *ab initio* potential energy surfaces and vibrational energies of H_2CS

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Six-dimensional (6D) potential energy surfaces (PESs) of H_2CS have been generated *ab initio* using the recently proposed explicitly correlated (F12) singles and doubles coupled cluster method including a perturbational estimate of connected triple excitations, CCSD(T)-F12b [T. B. Adler, G. Knizia, and H.-J. Werner, J. Chem. Phys. **127**, 221106 (2007)] in conjunction with F12-optimized correlation consistent basis sets. Core-electron correlation, high-order correlation, scalar relativistic, and diagonal Born-Oppenheimer terms were included as additive high-level (HL) corrections. The resulting 6D PESs were represented by analytical functions which were used in variational calculations of the vibrational term values below 5000 cm^{-1}. The best PESs obtained with and without the HL corrections, VQZ-F12^{*HL} and VQZ-F12*, reproduce the fundamental vibrational wavenumbers with mean absolute deviations of 1.13 and 1.22 cm^{-1}, respectively. A detailed analysis of the effects of the HL corrections shows how the VQZ-F12 results benefit from error cancellation. The present purely *ab initio* PESs will be useful as starting points for empirical refinements towards an accurate "spectroscopic" PES of H_2CS. © *2011 American Institute of Physics*. [doi:10.1063/1.3624570]

I. INTRODUCTION

Thioformaldehyde plays an important role in the photochemical evolution of sulfur-containing species in atmospheric and astrophysical chemistry (see, for example, Refs. 1–7). It was first detected in the laboratory by Johnson and Powell.[1] Soon thereafter, an interstellar search was carried out by Evans *et al.*,[2] which was followed by the first interstellar detection of H_2CS by Sinclair *et al.*[3] Woodney *et al.*[4] were the first to report the presence of H_2CS in the atmosphere of the comet Hale-Bopp. Recently, H_2CS was also identified in the Orion KL Nebula.[5–7]

Experimentally, there are only rather few high-resolution spectroscopic data on $H_2^{12}C^{32}S$ (henceforth referred to as thioformaldehyde or H_2CS). Recently, Flaud *et al.*[8] reported a high-resolution Fourier transform study of the infrared rovibrational spectrum of H_2CS at 10 μm, covering the ν_3, ν_4, and ν_6 vibrational bands. Maeda *et al.*[9] presented new laboratory measurements of the pure rotational spectrum of H_2CS together with a global analysis of all available experimental data on the rotational transitions. For the other three fundamental bands ν_1, ν_2, and ν_5, as well as for the overtone $2\nu_2$ and combination $\nu_2 + \nu_3$ bands, only low-resolution data have been published so far. Experimental work on H_2CS prior to 1983 has been reviewed by Clouthier and Ramsay.[10] A detailed up-to-date collection of the available experimental microwave, millimeter-wave, and far-infrared data on this molecule can also be found in the Cologne Database for molecular spectroscopy.[11,12] Concerning the electronic spectroscopy of H_2CS, experimental studies in the visible and ultraviolet regions were reported in Refs. 10 and 13–18.

On the theoretical side, the quartic force field for H_2CS was first calculated *ab initio* by Martin *et al.*[19] using the coupled cluster CCSD(T) method with a correlation-consistent triple-zeta basis set in the frozen core (FC) approximation: applying second-order perturbation theory,[20,21] the computed term values for the fundamental vibrations agreed with experiment to within 10 cm^{-1}, while variational VSCF-CI (Ref. 22) calculations gave vibrational term values for fundamental, overtone, and combination bands that are off by up to 20 cm^{-1}. The force field of Martin *et al.* was later refined by Carter and Handy[23] by fitting to the eight known vibrational ($J = 0$) and the corresponding ro-vibrational ($J = 1$) energy levels of H_2CS and D_2CS using their variational approach,[24] in which both the *ab initio* equilibrium geometry and force constants were adjusted. The corresponding root-mean-square (rms) errors were 0.4 cm^{-1} for the $J = 0$ vibrational band origins and 0.0044 cm^{-1} for the $J = 1$ energy levels (measured relative to the $J = 0$ level of the vibrational state in question).[23] This refined PES was recently employed in simulations of ro-vibrational spectra ($J \leq 20$) for H_2CS covering the pure rotational transitions as well as the ν_3, ν_4, and ν_6 bands;[25] the intensities were computed using a density functional theory dipole moment surface.[26]

The quality of an *ab initio* PES can usually be improved through fittings to accurate experimental energies or transition wavenumbers. The resulting so-called "spectroscopic" PES has the potential to approach experimental accuracy when used in variational (ro-)vibrational calculations. However, the scarcity of high-resolution spectroscopic data on H_2CS

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hinders the construction of an accurate "spectroscopic" PES for this molecule. For instance, the refined force constants from Carter and Handy[23] provide good accuracy for their fitting set (covering the pure rotational, fundamental, $2\nu_2$, and $\nu_2 + \nu_3$ bands), but cannot be expected to deliver the same accuracy for transitions beyond this set. In such a situation, accurate *ab initio* calculations are the only resort. Therefore, it is the goal of this paper to generate *ab initio* PESs for H_2CS by combining the highest level of modern *ab initio* theory with variational calculations of the vibrational energies for this molecule. Towards this end, we employ the recently proposed explicitly correlated F12 singles and doubles coupled cluster method including a perturbational estimate of connected triple excitations, CCSD(T)-F12b,[27] in conjunction with the corresponding F12-optimized correlation consistent basis sets. The F12 methods have the advantage to provide near-basis-set-limit accuracy already with basis sets of moderate size.[28] We also include high-level (HL) additive corrections for core-valence (CV) correlation, high-order electron correlation (HO), and scalar relativistic (SR) effects as well as diagonal Born-Oppenheimer corrections (DBOC). It has been shown in the case of diatomic closed-shell molecules that potential curves obtained from valence-only CCSD(T) calculations at the one-particle basis set limit can be improved by adding these HL corrections (even when evaluated with rather small basis sets), such that the desired spectroscopic accuracy is reached.[29–36] The importance of these corrections for accurate construction of multidimensional PESs of polyatomic molecules has also been recognized (see, for example, Refs. 37–42). We analyze in some detail the effect of the individual HL corrections on the vibrational term values of H_2CS below 5 000 cm^{-1}.

The paper is organized as follows. The *ab initio* calculations are presented in Sec. II A. The analytical representations of the individual HL contributions and of the total PES of H_2CS are described in Sec. II B. Section II C gives details on the variational calculations. The recommended PESs, their analysis, and comparisons with experiment are presented in Sec. III. Section IV offers some conclusions.

II. COMPUTATIONAL DETAILS

A. Electronic structure calculations

In the spirit of focal point analysis,[43] we use the following expression to represent the total electronic energy:

$$E_{\mathrm{tot}} = E_{\mathrm{fcCCSD(T)-F12}} + \Delta E_{\mathrm{CV}} + \Delta E_{\mathrm{HO}} + \Delta E_{\mathrm{SR}} + \Delta E_{\mathrm{DBOC}}, \tag{1}$$

where $E_{\mathrm{fcCCSD(T)-F12}}$ is the valence-only explicitly correlated coupled cluster CCSD(T)-F12 energy, ΔE_{CV} is the correction arising from core-valence correlation, ΔE_{HO} is the correction for electron correlation effects from higher order coupled cluster terms [beyond CCSD(T)], ΔE_{SR} accounts for scalar relativistic effects, and ΔE_{DBOC} is the diagonal Born-Oppenheimer correction. The energies from explicitly correlated CCSD(T) calculations, $E_{\mathrm{fcCCSD(T)-F12}}$, are known to converge much faster towards the basis set limit than those from the canonical CCSD(T) treatment. It has been shown, for example, that the accuracy of vibrational frequencies obtained from CCSD(T)-F12 in conjunction with triple-zeta basis sets matches the quality of the conventional CCSD(T) results with pentuple-zeta basis sets.[28]

To obtain the $E_{\mathrm{fcCCSD(T)-F12}}$ energies, we employed the recently proposed approximate explicitly correlated coupled cluster CCSD(T)-F12b (Ref. 27) method in conjunction with the diagonal fixed amplitude ansatz 3C(FIX) (Ref. 44) as implemented in the MOLPRO package of *ab initio* programs.[45] In this ansatz, the explicitly correlated amplitudes are determined utilizing the wave function cusp conditions. The method is orbital invariant, size consistent, and free from geminal basis set superposition errors.[44] For the efficient evaluation of the many-electron integrals in F12 theory, the resolution-of-identity (RI) approximation is combined with density fitting (DF). Therefore, the F12 calculations require three different basis sets for (i) orbitals, (ii) DF, and (iii) RI. In the present study, we employ the orbital basis sets specifically optimized for the F12 methods, namely, the valence correlation-consistent basis sets cc-pVTZ-F12 and cc-pVQZ-F12.[46] Henceforth, the corresponding explicitly correlated coupled cluster calculations as well as the resulting energies $E_{\mathrm{fcCCSD(T)-F12}}$ will be referred to as VTZ-F12 and VQZ-F12, respectively. We also utilized the OptRI,[47] cc-pV5Z/JKFIT,[48] and aug-cc-pwCV5Z/MP2FIT[49] auxiliary basis sets for evaluating the many-electron integrals (RI), the exchange and Fock operators (DF), and the remaining electron repulsion integrals (DF), respectively. The value of the geminal Slater exponent β was chosen as 1.0 both for VTZ-F12 and VQZ-F12 as recommended in Ref. 46.

In some calculations, we extrapolated the correlation part CCSD-F12b of $E_{\mathrm{fcCCSD(T)-F12}}$ to the complete basis set (CBS) limit utilizing the proposed X^{-7} and X^{-4} formulas, where $X = 3, 4$ denotes the cardinal quantum number of the basis sets VTZ-F12 and VQZ-F12, respectively. The choice of the X^{-7} extrapolating function is motivated by the formal convergence properties of explicitly correlated methods,[50,51] while the X^{-4} dependence conforms to the CBS extrapolation of the MP2-F12 correlation energies in a benchmark study for molecules containing first-row and some second-row atoms.[46] Since the perturbative triples (T) contributions to the correlation energies $E_{\mathrm{fcCCSD(T)-F12}}$ are not treated in an explicitly correlated manner in the current MOLPRO (Ref. 45) implementation, they were extrapolated using the standard X^{-3} expression.[52] We shall use the label VQZ-F12* for the results obtained by incorporating this CBS extrapolation for the (T) contributions on top of the VQZ-F12 results. In addition, the CBS extrapolation for the CCSD-F12b part is in some cases also included on top of the VQZ-F12* results, which leads to results denoted as CBS(7)-F12 and CBS(4)-F12, respectively, for the two types of extrapolating functions considered (see above). These latter two extrapolations for the CCSD-F12b part usually have only very minor effects (see below), and in the absence of further validation, it is not clear which one to prefer. Therefore, we adopt VQZ-F12* as our best approximation to the CCSD(T)/CBS limit. Adding all high-level corrections in their most accurate representation (see below) to VQZ-F12* yields the formally best surface denoted by VQZ-F12*HL.

The VTZ-F12 and VQZ-F12 energies were computed in the FC approximation. To estimate the effect of core-valence correlation ΔE_{CV}, we performed all-electron calculations, in which the $1s$ electrons of carbon and the $2s$ and $2p$ electrons of sulfur were correlated. The CCSD(T)-F12b method was used in conjunction with the core-valence basis sets cc-pCVTZ-F12 and cc-pCVQZ-F12 and the corresponding new compact RI auxiliary basis sets.[53] These CV calculations and the resulting energies will be referred to as $\text{CV}_{\text{TZ-F12}}$ and $\text{CV}_{\text{QZ-F12}}$, respectively, while CV will be used to label the correction irrespective of the basis set. We utilized the same DF auxiliary basis sets as in the FC calculations. The geminal Slater exponents β were selected as recommended in Ref. 53, namely, 1.4 ($\text{CV}_{\text{TZ-F12}}$) and 1.5 ($\text{CV}_{\text{QZ-F12}}$) both for the valence-only and all-electron calculations. In some calculations the $\text{CV}_{\text{TZ-F12}}$ and $\text{CV}_{\text{QZ-F12}}$ energies were extrapolated to the CBS limit (denoted as $\text{CV}_{\text{CBS(4)-F12}}$ and $\text{CV}_{\text{CBS(7)-F12}}$) using the same approach as in the extrapolation of the FC correlation energies (see above).

The SR corrections were computed using either the Cowan-Griffin perturbation theory[54] [including the one-electron Darwin and mass-velocity terms (MVD1)] or the second-order Douglas-Kroll-Hess (DKH2) approach,[55,56] with the former being included in the final PES. The MVD1 corrections were calculated at the all-electron CCSD(T) level of theory[57] employing the augmented core-valence aug-cc-pCVTZ basis set[58–61] as implemented in the program package CFOUR.[62] The DKH2 calculations were done with MOLPRO (Ref. 45) at the FC CCSD(T)/cc-pVQZ-DK level.[63] The DBOC corrections were determined using the aug-cc-pCVTZ basis set and the all-electron CCSD method[64] as implemented in CFOUR.[62]

The HO corrections were obtained from CCSDT, CCSDT(Q), CCSDTQ, and CCSDTQ(P) calculations that were performed with the general coupled cluster approach[65,66] implemented in the MRCC code[67] interfaced to CFOUR.[62] In these calculations, we employed the cc-pVDZ, aug-cc-pVnZ, and aug-cc-pV(n+d)Z (n = D,T) basis sets[58,59,68,69] [abbreviated as VDZ, AVnZ, and AV(n+d)Z, respectively] and the FC approximation. The corrections from the full triples [CCSDT-CCSD(T)] and the perturbative quadruples [CCSDT(Q)-CCSDT] were computed employing the AVTZ, AV(T+d)Z, and AVDZ, AV(D+d)Z basis sets, respectively. For the corrections from the full quadruples [CCSDTQ-CCSDT(Q)] and the perturbative pentuples [CCSDTQ(P)-CCSDTQ] the VDZ basis set was used.

B. Analytical representation of the potential energy surface

To generate an accurate multidimensional PES for a tetratomic molecule, a very large number of single-point *ab initio* calculations is required (several thousands at least). In our case, each *ab initio* point is constructed from five independent terms, see Eq. (1), each of which computationally very demanding. Our procedure of PES generation consists of the following three steps. (i) The first term, $E_{\text{fcCCSD(T)-F12}}$, is evaluated on the complete global grid of geometries (24 640 points). (ii) The other terms, i.e., the HL corrections, are computed on individually chosen (smaller) grids of geometries and described by suitable analytical functions that are usually rather simple, because the HL corrections are generally small and smooth (see below). (iii) The total energies are generated on the complete global grid of geometries by adding all terms, see Eq. (1), with the proviso that HL terms missing at any given grid point are determined by interpolation employing the corresponding analytical function from step (ii).

For the purpose of analysis, we compute not only a set of total energies according to Eq. (1), but in an analogous manner also sets of reduced energies, in which only individual HL terms are included (for example, VQZ-F12+CV, VQZ-F12+CV+HO, etc.); these are then used to investigate how different HL corrections and their combinations affect the vibrational energies. For each set of energies on the complete global grid, an analytical PES representation is constructed by fitting (see below) which serves as input for the variational calculation of the vibrational energies.

To make the required HL calculations feasible we adjusted the number of points in the corresponding grid depending on the target term E_{X} in Eq. (1) (X = CV, HO, SR, or DBOC). Towards this end, we set up four reduced grids designed to provide a reasonable description of each given term with minimum effort. Each of them was then interpolated independently by fitting to an appropriate analytical function. In fact, the HL corrections in Eq. (1) are quite distinct in terms of their dependence on the internal coordinates of the molecule. This is illustrated in Figs. 1 and 2, where one-dimensional (1D) cuts are shown for different HL terms. In general, the CV and particularly the HO terms appear to be larger than the MVD1 and DBOC terms, and their variation is usually more pronounced along the stretching modes (especially the C–S bond) than along the bending modes. Most of the HL corrections show a rather simple polynomial-type dependence along the cuts. Thus, we could reduce the number of required expansion parameters (force constants) as well as the number of the corresponding *ab initio* data points by individually selecting an appropriate analytical form for each HL term. Towards this end, we tested different types of vibrational coordinates and found that the valence coordinates (see the definition below) provide the highest degree of inter-mode separation, at least in the energy range below 20 000 cm^{-1}.

To construct a six-dimensional (6D) analytical representation for the HL correction energies E_{X} (X = CV, HO, MVD1, and DBOC) in Eq. (1), the following n-mode expansion was used as

$$\mathcal{F} = \mathcal{F}^{(0)} + \sum_{i}^{6} \mathcal{F}_i^{(1)}(\xi_i) + \sum_{i}^{6}\sum_{i>j}^{6} \mathcal{F}_{ij}^{(2)}(\xi_i,\xi_j) + \sum_{i}^{6}\sum_{i>j}^{6}\sum_{i>j>k}^{6} \mathcal{F}_{ijk}^{(3)}(\xi_i,\xi_j,\xi_k) + \cdots, \tag{2}$$

where $\mathcal{F}_{ijk\ldots}^{(n)}(\xi_i,\xi_j,\xi_k,\ldots)$ is a n-dimensional cut ($n = 1,\ldots,6$) through the corresponding six-dimensional surface E_{X} along the $\xi_i,\xi_j,\xi_k,\ldots$ coordinates, with all other coordinates fixed to zero. In turn, each n-mode term in

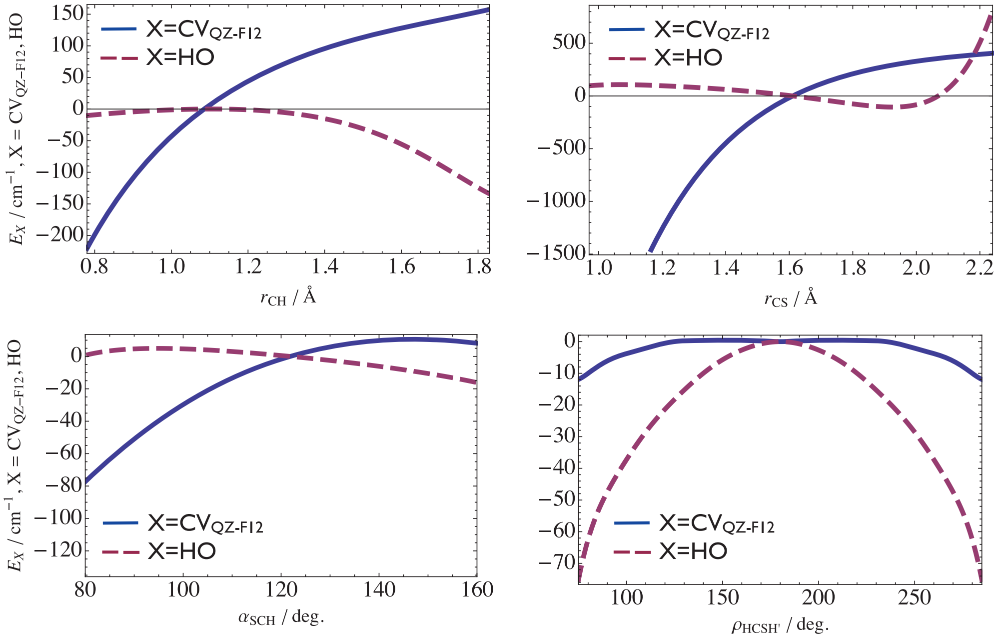

FIG. 1. One-dimensional cuts of the $\mathrm{CV_{QZ-F12}}$ and HO corrections given by the solid and dashed lines, respectively. The ranges for the coordinates are selected, such that the total energy is always below 25 000 cm^{-1}. Please note the different energy scales.

Eq. (2) is given by the polynomial expansion

$$\mathcal{F}^{(n)}_{ij..}(\xi_i, \xi_j, ...) = \sum_{s>0,t>0,...} F^{(ij...)}_{st...}\xi_i^s \xi_j^t ... \qquad (3)$$

in terms of the variables

$$\xi_i = r_i - r_i^{(\mathrm{eq})}, \quad i = \mathrm{CS},\ \mathrm{CH_1},\ \text{or}\ \mathrm{CH_2}, \qquad (4)$$

$$\xi_j = \alpha_j - \alpha_j^{(\mathrm{eq})}, \quad j = \mathrm{SCH_1}\ \text{or}\ \mathrm{SCH_2}, \qquad (5)$$

$$\xi_6 = 1 + \cos\rho. \qquad (6)$$

Here, r_{CS}, $r_{\mathrm{CH_1}}$, and $r_{\mathrm{CH_2}}$ are the bond lengths, $\alpha_{\mathrm{SCH_1}}$ and $\alpha_{\mathrm{SCH_2}}$ are the bond angles, and ρ is the dihedral angle between the SCH$_1$ and SCH$_2$ planes. The expansion coefficients $F^{(ij...)}_{st...}$ in Eq. (3) obey the permutation rule

$$F^{(i'j'...)}_{st...} = F^{(ij...)}_{st...}, \qquad (7)$$

where the indices i', j'... are obtained from i, j... by replacing all indices 2 by 3, all indices 3 by 2, all indices 4 by 5, and all indices 5 by 4.

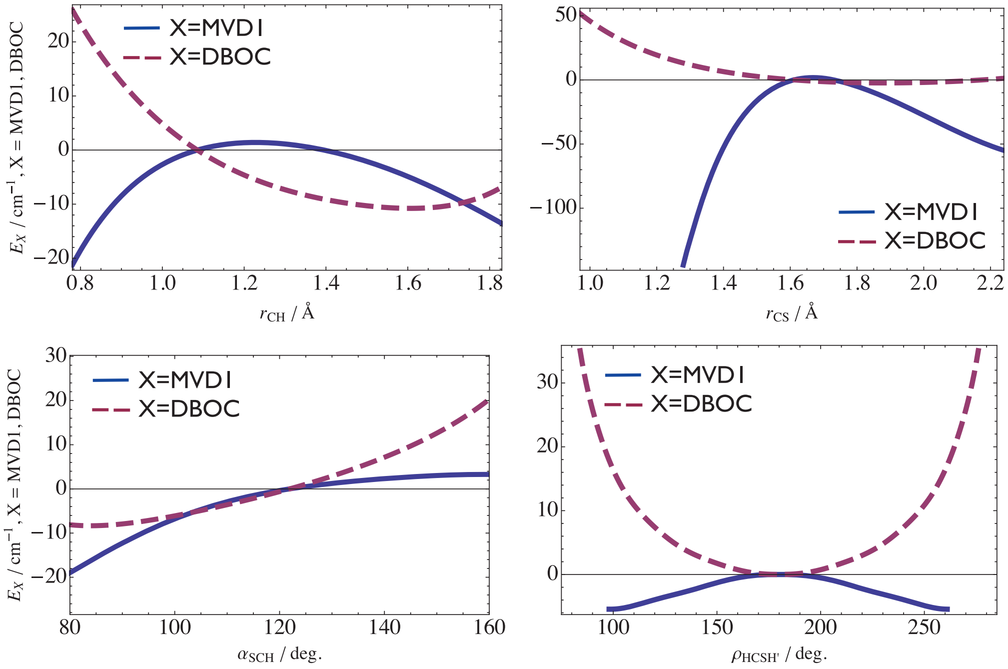

FIG. 2. One-dimensional cuts of the MVD1 and DBOC corrections given by the solid and dashed lines, respectively. The ranges for the coordinates are selected, such that the total energy is always below 25 000 cm^{-1}. Please note the different energy scales.

The linear expansion coefficients $F^{(ij\ldots)}_{st\ldots}$ in Eq. (3) were determined for each HL term independently by a least-squares fit (LSQ) to the corresponding *ab initio* data points. The GESVD routine from LAPACK was used to solve the corresponding (ill-conditioned) LSQ system of linear equations by the singular value decomposition technique. For each HL term we determined two to three interpolating polynomials, depending on the truncation order ($n_{\max} = 2$, 3, or 4) in the n-mode expansion (2). The maximum expansion order in Eq. (3) was restricted to six. For different HL terms the number of *ab initio* points varied between 700 and 5000 depending on $n_{\max}$. In case of the 2-mode expansions, we could usefully vary 143, 135, 138, 193, 68, and 97 parameters for the $\mathrm{CV_{TZ-F12}}$, $\mathrm{CV_{QZ-F12}}$, HO, DKH2, MVD1, and DBOC terms, respectively, while 196, 187, 194, 230, 134, and 200 parameters were used for the 3-mode expansions. The 4-mode expansion was employed only for the $\mathrm{CV_{TZ-F12}}$, $\mathrm{CV_{QZ-F12}}$, DKH2, and MVD1 corrections, utilizing 221, 214, 315, and 96 parameters, respectively. The rms errors in all these fittings were less than 0.1 $\mathrm{cm^{-1}}$.

The VQZ-F12 total energies and the various types of CBS corrections to the FC correlation energies were calculated on a grid containing 7647 geometries. The energy differences $E_{\mathrm{VQZ-F12}} - E_{\mathrm{VTZ-F12}}$ and the CBS corrections ($E_{\mathrm{VQZ-F12^*}} - E_{\mathrm{VQZ-F12}}$ or $E_{\mathrm{CBS-F12}} - E_{\mathrm{VQZ-F12}}$) were represented by the same kind of n-mode expansion that was also used for the HL corrections, Eq. (2). The 4-mode expansion was employed to fit the $E_{\mathrm{VQZ-F12}} - E_{\mathrm{VTZ-F12}}$, $E_{\mathrm{VQZ-F12^*}} - E_{\mathrm{VQZ-F12}}$, $E_{\mathrm{CBS(7)-F12}} - E_{\mathrm{VQZ-F12}}$, and $E_{\mathrm{CBS(4)-F12}} - E_{\mathrm{VQZ-F12}}$ basis set corrections utilizing 485, 493, 73, and 166 parameters, respectively. The rms errors in these fittings were less than 0.15 $\mathrm{cm^{-1}}$.

The CCSD(T) energies $E_{\mathrm{fcCCSD(T)-F12}}$ [first term in Eq. (1)] were generated as follows: the VTZ-F12 energies were calculated directly on the global grid for each of the 24 640 points (up to 40 000 $\mathrm{cm^{-1}}$), the VQZ-F12 energies were then obtained by adding the energy differences $E_{\mathrm{VQZ-F12}} - E_{\mathrm{VTZ-F12}}$ as evaluated at each grid point either directly (at 7647 geometries) or from the corresponding n-mode expansion, and the CBS corrections were included in the same manner. The total energies E_{tot}, see Eq. (1), were obtained for each grid point likewise, by adding the HL corrections calculated either directly or from their n-mode expansions (2).

The convergence of the HL terms with respect to the expansion order $n_{\max}$ in the n-mode expansion (2) is illustrated in Fig. 3, where we show the following rms deviations as a function of the total energy $E = E_{\mathrm{tot}}$,

$$\sigma_{\mathrm{X}}(E) = \sqrt{\sum_{i}^{N} \left[E_{\mathrm{X}}^{(n_{\max}+1)}(i) - E_{\mathrm{X}}^{(n_{\max})}(i)\right]^2 / N}. \tag{8}$$

Here, i runs over all 24 640 geometries of the global grid, and $\mathrm{X} = \mathrm{CV_{QZ-F12}}$, HO, MVD1, and DBOC. The main features in the plots for $\mathrm{CV_{TZ-F12}}$ and DKH2 resemble those for $\mathrm{CV_{QZ-F12}}$ and MVD1, respectively, and are thus not shown. As can be seen from Fig. 3, the differences between the interpolated energies $E_{\mathrm{X}}^{(4)}$ and $E_{\mathrm{X}}^{(3)}$ are small for $\mathrm{X} = \mathrm{CV_{QZ-F12}}$ and MVD1, of the order of 0.1 $\mathrm{cm^{-1}}$ (circles). For X = HO and DBOC, where only the 2- and 3-mode expansions were feasible computationally, the differences between the interpolated energies $E_{\mathrm{X}}^{(3)}$ and $E_{\mathrm{X}}^{(2)}$ are of similar magnitude as those for $\mathrm{X} = \mathrm{CV_{QZ-F12}}$ and MVD1 (squares), and one may thus assume an analogous convergence behavior. Hence, the use of 3- or 4-mode expansions in Eq. (2) should be sufficient to obtain well-converged energies for all HL corrections. In the energy region above 14 000 $\mathrm{cm^{-1}}$, the CCSD(T) energies of H_2CS start to become non-smooth which leads to a step-like increase (of up to 0.5 $\mathrm{cm^{-1}}$) in all rms plots in Fig. 3. The apparent convergence of the rms errors above 20 000 $\mathrm{cm^{-1}}$ is due to the limited number of calculated *ab initio* data at high energies.

We have also investigated how the different HL corrections as well as their analytical representations affect the vibrational energies. Towards this end, we have generated a number of PESs resulting from different n-mode expansions in combination with different HL terms (13 in total), such as VQZ-F12+$\mathrm{X}^{(n_{\max}=2)}$, VQZ-F12+$\mathrm{X}^{(n_{\max}=3)}$, VQZ-F12+$\mathrm{X}^{(n_{\max}=4)}$, etc. (X = CV, HO, SR, and DBOC). The vibrational energies were then computed variationally using the program TROVE (Ref. 70) (see below). The convergence of the vibrational term values with respect to the expansion order $n_{\max}$ in Eq. (2) is illustrated in Figs. 4 and 5, which show the differences between the vibrational energies obtained with the 2- and 3-mode expansions (bars) and with the 3- and 4-mode expansions (circles), respectively. We conclude that the 3-mode expansion is sufficient to obtain vibrational term values converged to better than 0.1 $\mathrm{cm^{-1}}$.

To construct an accurate analytical representation for the total energy, Eq. (1), we follow Ref. 41 and divide the PES into short-range and long-range terms

$$V = V_{\mathrm{short}} f_{\mathrm{damp}} + V_{\mathrm{long}}. \tag{9}$$

The long-range part V_{long} is given by a simple Morse potential in terms of the three stretching coordinates

$$V_{\mathrm{long}} = \sum_{i=1}^{3} D_{\mathrm{e}}^{(i)} [1 - \exp(-a_i \Delta r_i)]^2, \tag{10}$$

where $\Delta r_i = r_i - r_i^{(\mathrm{ref})}$ and $i = \mathrm{CS}, \mathrm{CH_1}$, or $\mathrm{CH_2}$. The parameters $D_{\mathrm{e}}^{(i)}$ and a_i are selected to provide the correct asymptotic behavior of the potential energy in the corresponding dissociation channel. The f_{damp} function which "damps" the short-range potential at large displacements of the nuclei is given by

$$f_{\mathrm{damp}} = \exp\left(\sum_{i=1}^{3} -d_i \Delta r_i^4\right). \tag{11}$$

The criteria used for choosing the damping parameters d_i are (i) small rms errors and (ii) smooth behavior of the resulting potential function along each 1D dissociation cut. The short-range part of the PES is represented by a six-mode eight-order expansion, as given in Eqs. (2) and (3). To investigate the effects of the individual HL correction terms on the equilibrium constants and vibrational energies we have constructed

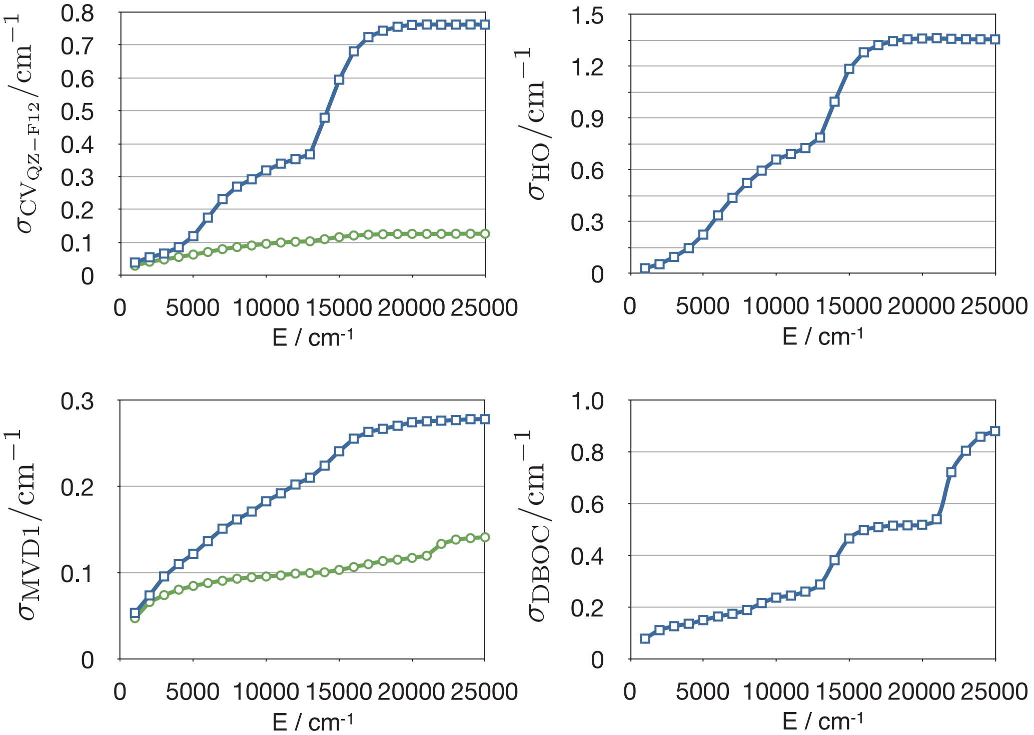

FIG. 3. Estimates of rms fitting errors, Eq. (8), for the HL corrections as function of the total energy: n-mode expansions for $n_{\max} = 2$ (squares) and $n_{\max} = 3$ (circles). Please note the different energy scales.

several six-dimensional PESs with different HL contributions (see above). The expansion parameters were determined by a LSQ fit to the 24 640 energies calculated in accordance with Eq. (1). The number of parameters varied between 800 and 900 depending on the individual case. The rms errors were less than 0.2 cm^{-1} in all these fittings. In case of the total energy, E_{tot}, we used the weighting function suggested by Partridge and Schwenke,[71]

$$w_i = \left\{1\big/E_i^{(w)} \tanh\left[-0.0006\,(E_i - 40\,000)\right] + 1.002\,002\,002\right\}\big/2.002\,002\,002, \qquad (12)$$

where $E_i^{(w)} = \max(20\,000,\, E_i)$ and E_i is the energy at the ith geometry (all values in cm^{-1}). Thus points below 20 000

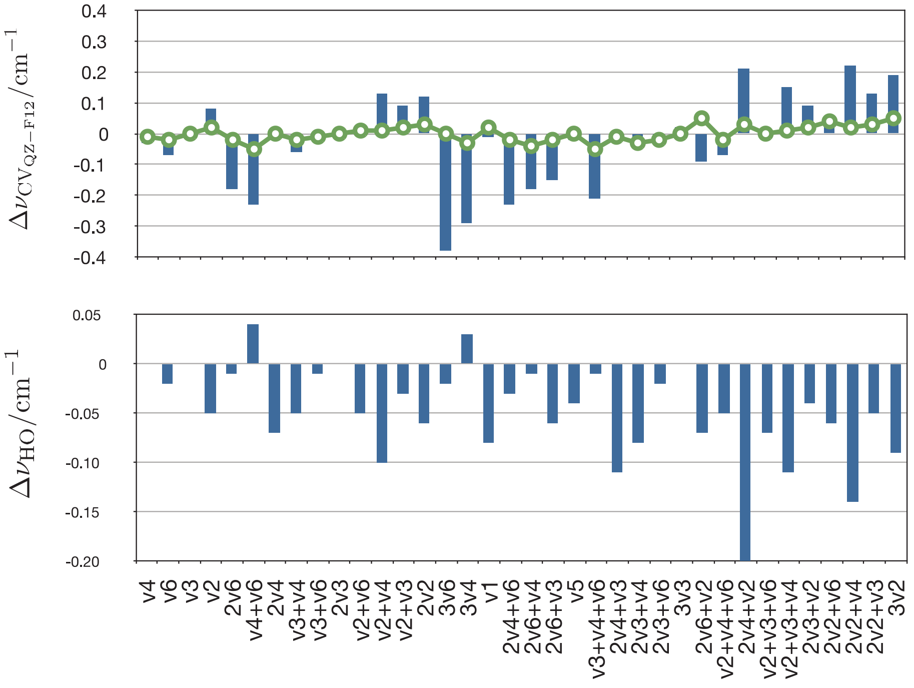

FIG. 4. Convergence of the vibrational term values (see Table III) of H_2CS with respect to the truncation order in the n-mode expansions of different HL corrections: $\Delta\nu_{\mathrm{X}} = \nu_{\mathrm{X}}^{(n_{\max}+1)} - \nu_{\mathrm{X}}^{(n_{\max})}$ (X = CV and HO) for $n_{\max} = 2$ (bars) and $n_{\max} = 3$ (circles). Please note the different energy scales.

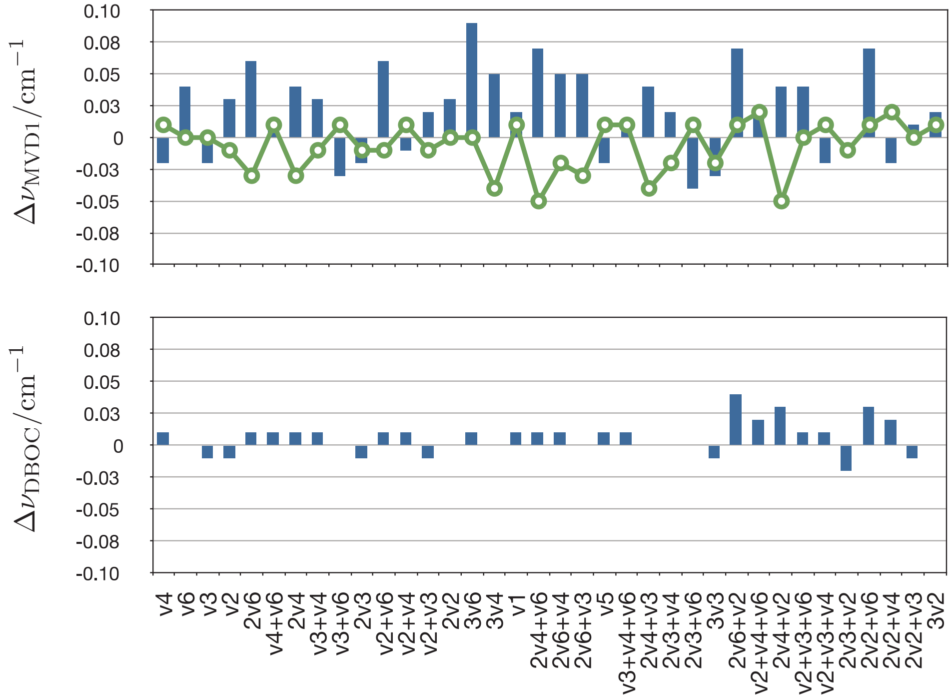

FIG. 5. Convergence of the vibrational term values (see Table III) of H_2CS with respect to the truncation order in the n-mode expansions of different HL corrections: $\Delta\nu_X = \nu_X^{(n_{\max}+1)} - \nu_X^{(n_{\max})}$ (X = MVD1 and DBOC) for $n_{\max} = 2$ (bars) and $n_{\max} = 3$ (circles).

cm^{-1} are weighted more heavily. All potential parameters for our two recommended surfaces, VQZ-F12* and VQZ-F12*$^{\mathrm{HL}}$, are given in the supplementary material.[72] The rms errors were less than 0.2 cm^{-1} in these two final fits.

C. Variational calculations of vibrational energies

We computed the vibrational energies of H_2CS employing the variational program TROVE.[70] In TROVE, the kinetic energy and potential energy operators are represented by Taylor series expansions of the Xth and Yth order, respectively, in coordinates ξ_i^ℓ. The HL effects on the vibrational energies as well as their n-mode convergence were studied employing X = 6 and Y = 8, while our best estimates for vibrational energies were obtained with X = 8 and Y = 12. The coordinates ξ_i^ℓ $(i = 1, \ldots, 5)$ are linearized versions[73] of the coordinates ξ_i defined in Eqs. (4) and (5). The dihedral angle ρ is treated as a nonrigid mode, i.e., it is evaluated explicitly on a grid of equidistantly spaced values.[70] The size of the vibrational basis set, and therefore the size of the Hamiltonian matrix, is controlled by the polyad number P, which in the present case is given by

$$P = n_1 + 2(n_2 + n_3) + n_4 + n_5 + n_6, \tag{13}$$

where the local-mode quantum numbers n_i are defined in connection with the primitive basis functions ϕ_{n_i} (see Ref. 70 for details). Hence, we include in the primitive basis set only those combinations of ϕ_{n_i} for which $P \leq P_{\max}$. In the present work, we use $P_{\max} = 18$, which ensures convergence to better than 0.1 cm^{-1} for vibrational energies below 5000 cm^{-1}.

We use the normal mode quantum numbers v_1, v_2, v_3, v_4, v_5, and v_6 to label the vibrational states of H_2CS as $v_1\nu_1 + v_2\nu_2 + v_3\nu_3 + v_4\nu_4 + v_5\nu_5 + v_6\nu_6$. The normal modes are defined as follows. Here, ν_1 is the symmetric C–H stretching mode (2971.03 cm^{-1}), ν_2 is the symmetric S–C–H bending mode (1455.50 cm^{-1}), ν_3 is the C–S stretching mode (1059.21 cm^{-1}), ν_4 is the out-of-plane bending mode (990.18 cm^{-1}), ν_5 is the asymmetric C–H stretching mode (3024.62 cm^{-1}), and ν_6 is the asymmetric S–C–H bending mode (991.02 cm^{-1}). The values given in parentheses are the experimental fundamental frequencies from Ref. 10.

III. RESULTS

Here, we first analyze how different levels of *ab initio* theory affect the calculated equilibrium geometry and harmonic frequencies of H_2CS. The results of this analysis are summarized in Tables I and II, where our calculated values are compared with the published experimental data and previous theoretical results.

The equilibrium geometry of H_2CS obtained at the VQZ-F12 level of theory is in good agreement with experiment: the theoretical CS and CH equilibrium bond distances of 161.21 and 108.67 pm are only slightly larger, by 0.11 pm, than the experimentally derived equilibrium values.[74] The basis set convergence of the equilibrium parameters is very fast: going from VTZ-F12 to VQZ-F12 changes their values by only –0.04 pm (CS), –0.02 pm (CH), and 0.0005°(HCS). The corresponding effect on the harmonic frequencies is less than 1.4 cm^{-1} in all cases. Further extrapolation to the CBS limit results in very small variations both in the equilibrium bond lengths (within 0.02 pm) and harmonic frequencies (within 1 cm^{-1}). Therefore, both VQZ-F12 and VQZ-F12* can serve as reference methods that provide results of essentially CCSD(T)/CBS quality.

TABLE I. Equilibrium constants of H_2CS (see text for notation). Increments from basis set extension and high-level corrections are given with respect to the VTZ-F12 reference structure.

	CS, pm	CH, pm	HCS, deg.
VTZ-F12	161.25	108.69	121.79
VQZ-F12	–0.04	–0.02	0.00
VQZ-F12*	–0.02	–0.02	0.00
CBS(7)-F12	–0.04	–0.02	0.00
CBS(4)-F12	–0.05	–0.02	0.00
CV_{TZ-F12}	–0.42	–0.15	0.00
CV_{QZ-F12}	–0.44	–0.15	0.00
$CV_{CBS(7)-F12}$	–0.44	–0.15	0.00
$CV_{CBS(4)-F12}$	–0.45	–0.15	0.00
HO	0.12	0.00	0.00
DKH2	–0.02	–0.01	–0.01
MVD1	–0.02	–0.01	–0.01
DBOC	0.01	0.02	–0.01
Our best estimate[a]	160.90	108.53	121.77
Refined PES (Ref. 23)	161.10	108.56	121.88
Experimentally derived (Ref. 74)	161.10(8)	108.56(21)	

[a] VQZ-F12*+CV_{QZ-F12}+HO+MVD1+DBOC.

Regarding the contributions from the HL corrections, the largest effect is observed for CV. For example, the CS equilibrium bond is shortened by about 0.44 pm, and the harmonic frequencies ω_1 and ω_5 are increased by 6.2 cm^{-1}, when the CV terms are taken into account. The CV correction exhibits very fast convergence in terms of the basis set (VTZ-F12 $\longrightarrow$VQZ-F12): the maximum changes in the equilibrium distances and harmonic frequencies are found for $r_{CS}^{(eq)}$ (0.02 pm) and ω_3 (0.3 cm^{-1}), respectively. The CBS extrapolation leads to negligible modifications both of the equilibrium distances (less than 0.01 pm) and harmonic frequencies (less than 0.1 cm^{-1}).

In H_2CS, the effect of the CV correction on the harmonic frequencies is largely compensated by the effects of the other three HL corrections considered presently (i.e., HO+SR+DBOC with SR = MVD1 or DKH2). While the CV correction affects mainly the CH stretching modes, the HO and SR corrections influence especially the CS stretching mode.

TABLE II. Harmonic frequencies (in cm^{-1}) of H_2CS (see text for notation). Increments from basis set extension and high-level corrections are given with respect to the VTZ-F12 reference value.

	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6
VTZ-F12	3083.26	1495.91	1076.42	1002.36	3175.09	1004.48
VQZ-F12	1.18	–0.69	0.60	1.18	1.40	–0.75
VQZ-F12*	0.83	–1.48	0.29	0.64	1.17	–1.08
CBS(7)-F12	1.01	–1.42	0.47	0.72	1.35	–1.13
CBS(4)-F12	1.40	–1.50	0.82	0.74	1.83	–0.70
CV_{TZ-F12}	6.05	2.75	4.67	3.87	6.07	2.64
CV_{QZ-F12}	6.21	2.95	4.93	3.85	6.17	2.84
$CV_{CBS(7)-F12}$	6.21	2.98	4.93	3.77	6.17	2.85
$CV_{CBS(4)-F12}$	6.26	3.05	5.03	3.80	6.22	2.92
HO	–0.89	–1.05	–4.58	–3.43	–1.01	–1.05
DKH2	–0.45	–0.21	–1.46	–0.43	–0.31	–0.43
MVD1	–0.52	–0.17	–1.47	–0.33	–0.34	–0.34
DBOC	–0.65	–0.26	–0.07	–0.21	–0.40	0.07
Total correction[a]	4.15	1.47	–1.19	–0.12	4.42	1.52
Our best estimate[b]	3088.24	1495.90	1075.52	1002.88	3180.68	1004.92

[a] CV_{QZ-F12}+HO+MVD1+DBOC.
[b] VQZ-F12*+CV_{QZ-F12}+HO+MVD1+DBOC.

The formally highest *ab initio* level in the present work is reached by supplementing the VQZ-F12* energies with all HL corrections (i.e., VQZ-F12* +CV_{QZ-F12}+HO+MVD1+DBOC). At this VQZ-F12^{*HL} level, the equilibrium constants deviate from the experimentally derived values by –0.20 pm, –0.03 pm, and –0.11°for r_{CS}, r_{CH}, and α_{SCH}, respectively; these deviations are comparable to those at the VQZ-F12* level (+0.13 pm, +0.11 pm, and −0.09°). For the harmonic frequencies of H_2CS, there are no reliable experimental values for comparison. Inclusion of all HL corrections increases the harmonic CH stretching wavenumbers ω_1 and ω_5 by 4.2 and 4.4 cm^{-1}, respectively, while the changes for the other fundamental modes range between 0.1 and 1.5 cm^{-1}.

We now turn to a discussion of the variational results for the vibrational term values below 5000 cm^{-1}. We first address their convergence with regard to the basis set used in the CCSD(T) calculations [first term in Eq. (1)]. Figure 6 shows the changes in the computed term values upon basis set extension or extrapolation. Generally speaking, these changes are rather small, typically of the order of 1–2 cm^{-1}, so that basis set convergence is fast. At the CCSD(T)-F12b level, the differences between VQZ-F12 and VTZ-F12 (columns) tend to be most notable for modes involving ν_3 – they exceed 2.0 cm^{-1} for two such modes. Going beyond VQZ-F12, there is a well-validated extrapolation strategy for the perturbative triples (T) energy contributions in canonical CCSD(T) calculations.[52] The resulting (T) CBS corrections relative to VQZ-F12 (grey area in Fig. 6) generally lower the term values slightly, by about 1 cm^{-1}. Since they come from an established procedure, we have included them in our final CCSD(T) energies (labeled as VQZ-F12*). They are also incorporated in the remaining two curves that indicate the additional changes in the CCSD-F12b contributions arising from the X^{-7} and X^{-4} extrapolations (squares and circles, respectively, in Fig. 6). These two curves follow the same pattern, but they often differ appreciably, and it is not clear which one to prefer. The shifts due to the X^{-7} extrapolation for the CCSD part are tiny (squares vs. grey curve) whereas those due to the X^{-4} extrapolation are slightly larger (circles vs. grey curve), but mostly still small on an absolute scale. Since none of these two extrapolation procedures for the CCSD part is firmly established, we have decided against incorporating either of these two corrections. For the CCSD contribution to our PES, we thus adopt the VQZ-F12 energies, which have previously been shown to yield results of nearly benchmark quality.[28,35]

Table III lists the VQZ-F12* results, the changes resulting from the different HL corrections, and the total changes upon inclusion of all four HL corrections. The CV terms cause a substantial increase in the computed wavenumbers, up to 15 cm^{-1} in overtone and combination bands, and up to 6–7 cm^{-1} in the fundamental bands (CH stretching modes). This increase is largely compensated by the strong decrease

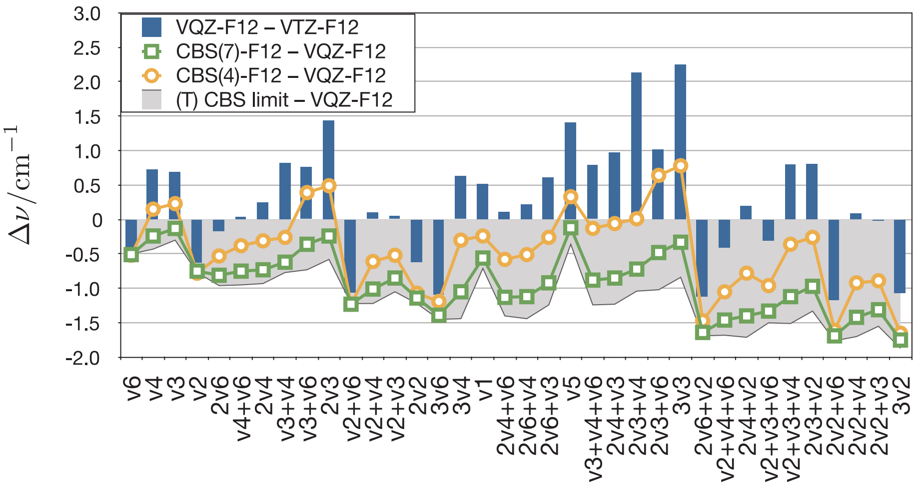

FIG. 6. Basis set convergence of the CCSD(T)-F12b vibrational term values (in cm^{-1}) of H_2CS. The grey area shows the changes due to the CBS extrapolation of the perturbative triples (T) contributions relative to VQZ-F12 (see text).

TABLE III. The effect of the high-level *ab initio* corrections on the vibrational term values (in cm^{-1}) of H_2CS.

Mode	$\Gamma^{(C_{2v})}$	VQZ-F12*	CV_{QZ-F12}	HO	MVD1	DKH2	DBOC	Total[a]
ν_6	B_2	989.59	2.71	−1.19	−0.35	−0.43	0.09	1.26
ν_4	B_1	990.59	3.64	−3.01	−0.56	−0.51	−0.03	0.04
ν_3	A_1	1061.81	4.94	−4.61	−1.48	−1.46	−0.05	−1.20
ν_2	A_1	1454.50	2.89	−1.28	−0.19	−0.24	−0.20	1.22
$2\nu_6$	A_1	1965.56	6.03	−3.84	−0.89	−0.91	0.10	1.40
$\nu_4+\nu_6$	A_2	1988.41	6.33	−4.22	−0.92	−0.93	0.08	1.27
$2\nu_4$	A_1	1991.73	6.50	−4.45	−0.93	−0.92	0.01	1.13
$\nu_3+\nu_4$	B_1	2047.29	7.65	−6.15	−2.03	−1.96	−0.09	−0.62
$\nu_3+\nu_6$	B_2	2047.92	8.63	−7.43	−1.84	−1.90	0.04	−0.60
$2\nu_3$	A_1	2113.97	9.88	−9.25	−2.95	−2.90	−0.12	−2.44
$\nu_2+\nu_6$	B_2	2429.00	5.49	−2.45	−0.54	−0.66	−0.12	2.38
$\nu_2+\nu_4$	B_1	2438.82	6.63	−4.47	−0.79	−0.78	−0.23	1.14
$\nu_2+\nu_3$	A_1	2511.92	7.84	−5.92	−1.66	−1.69	−0.26	0.00
$2\nu_2$	A_1	2875.24	5.71	−2.25	−0.46	−0.51	−0.44	2.56
$3\nu_6$	B_2	2946.96	8.40	−4.52	−1.12	−1.28	0.26	3.02
$3\nu_4$	B_1	2954.65	9.94	−7.55	−1.52	−1.39	0.02	0.89
ν_1	A_1	2969.47	6.11	−2.04	−0.52	−0.50	−0.56	2.99
$2\nu_4+\nu_6$	B_2	2997.92	9.32	−6.06	−1.35	−1.34	0.06	1.97
$2\nu_6+\nu_4$	B_1	3000.08	9.70	−6.66	−1.40	−1.39	0.04	1.68
$2\nu_6+\nu_3$	A_1	3018.97	10.69	−8.30	−2.38	−2.38	0.05	0.06
ν_5	B_2	3024.32	6.54	−2.28	−0.50	−0.46	−0.34	3.42
$\nu_3+\nu_4+\nu_6$	A_2	3041.58	11.32	−8.99	−2.40	−2.40	0.03	−0.04
$2\nu_4+\nu_3$	A_1	3044.92	11.47	−9.18	−2.42	−2.39	−0.03	−0.16
$2\nu_3+\nu_6$	B_2	3095.45	13.60	−11.61	−3.31	−3.41	−0.02	−1.34
$2\nu_3+\nu_4$	B_1	3095.51	12.56	−11.36	−3.51	−3.34	−0.14	−2.45
$3\nu_3$	A_1	3156.42	14.81	−13.89	−4.42	−4.34	−0.16	−3.66
$2\nu_6+\nu_2$	A_1	3393.66	8.42	−4.35	−0.95	−1.09	−0.06	3.06
$\nu_2+\nu_4+\nu_6$	A_2	3422.46	9.23	−5.64	−1.16	−1.20	−0.12	2.31
$2\nu_4+\nu_2$	A_1	3429.48	9.92	−6.82	−1.31	−1.25	−0.24	1.55
$\nu_2+\nu_3+\nu_6$	B_2	3482.65	10.43	−7.15	−2.02	−2.12	−0.17	1.09
$\nu_2+\nu_3+\nu_4$	B_1	3491.57	11.62	−9.20	−2.28	−2.24	−0.29	−0.15
$2\nu_3+\nu_2$	A_1	3559.70	12.77	−10.58	−3.13	−3.13	−0.32	−1.26
$2\nu_2+\nu_6$	B_2	3839.77	8.26	−3.52	−0.78	−0.91	−0.34	3.62
$2\nu_2+\nu_4$	B_1	3855.66	9.50	−5.56	−1.07	−1.07	−0.46	2.41
$2\nu_2+\nu_3$	A_1	3930.76	10.64	−6.92	−1.93	−1.96	−0.49	1.30
$3\nu_2$	A_1	4283.46	8.50	−3.43	−0.70	−0.78	−0.63	3.74

[a] CV_{QZ-F12}+HO+MVD1+DBOC.

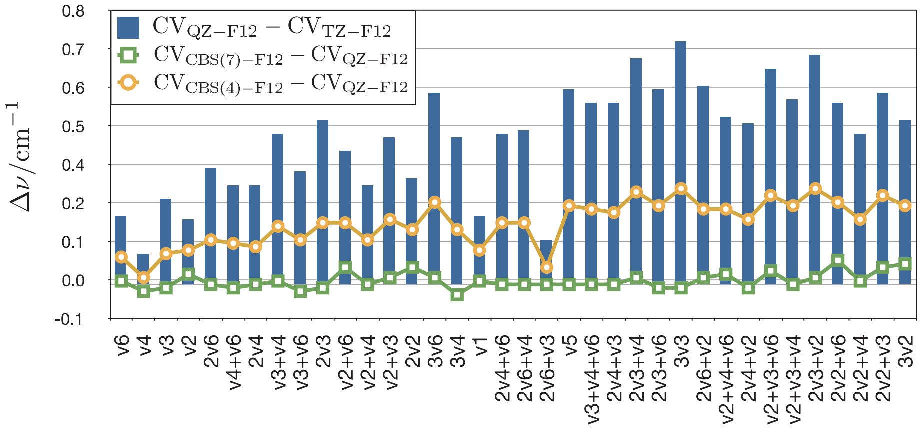

FIG. 7. Basis set convergence of the CV effects on the vibrational term values (in cm^{-1}) of H$_2$CS.

coming mainly from the HO terms, up to –14 cm^{-1} in overtone and combination bands, and up to –5 cm^{-1} in the fundamental bands (CS stretching mode), with further smaller negative contributions from the relativistic terms, up to –4.4 cm^{-1}. The two alternative approaches for computing the relativistic effects (MVD1 and DKH2) yield quite similar results: they lower the computed wavenumbers typically by 1–2 cm^{-1}, with somewhat larger effects on modes that involve CS stretching (ν_3 and its overtone and combination bands). The DBOC correction affects mostly only the ν_1 and ν_5 modes, but its influence is generally small (normally less than 0.5 cm^{-1}). Because of cancellation effects, the HL corrections cause only a rather small overall shift in the calculated wavenumbers, with a maximum shift of 3.7 cm^{-1} in the 3ν_2 overtone. The fundamental CH stretching modes are among the few examples where this compensation is fairly incomplete, since the large positive CV contributions outweigh the negative HO and SR contributions, leading to overall shifts of 3.0 cm^{-1} for ν_5 and 3.4 cm^{-1} for ν_5. For the other four fundamentals, the overall shifts are small and do not exceed 1.3 cm^{-1}.

We have also checked the basis set dependence for the largest HL correction, i.e., the CV contribution (see Fig. 7). The basis set extension TZ→QZ causes the computed vibrational term values to change by less than 1 cm^{-1} (with a maximum value of 0.7 cm^{-1} for 3ν_3). The CBS extrapolation of the $\mathrm{CV_{QZ-F12}}$ energies only leads to tiny modifications of the vibrational term values, less than 0.2 cm^{-1} for $\mathrm{CV_{CBS(4)-F12}}$ and 0.1 cm^{-1} for $\mathrm{CV_{CBS(7)-F12}}$.

We now focus on our two recommended *ab initio* PESs of H$_2$CS, obtained without (VQZ-F12*) and with (VQZ-F12$^{*\mathrm{HL}}$) the HL corrections. Both PESs are of similar quality because the HL corrections compensate each other to a large extent (see above). Table IV lists the fundamental term values obtained with these two PESs and compares them to the available experimental data.[8,10] The VQZ-F12* surface provides vibrational term values in fairly good agreement with experiment: the maximum error is 2.60 cm^{-1} for ν_3, the deviations are less than 2 cm^{-1} for the other fundamentals, and the mean absolute deviation for all six fundamentals amounts to 1.22 cm^{-1} (the latter is even lower for the VQZ-F12 surface, 0.97 cm^{-1}). In spite of the significantly higher computational effort, the VQZ-F12$^{*\mathrm{HL}}$ surface yields similar errors: the wavenumbers of the C–H stretching modes ν_1 and ν_5 are overestimated by 1.43 and 3.12 cm^{-1}, respectively, the description of ν_3 is slightly improved (overestimate of 1.40 rather than 2.60 cm^{-1}), and the mean absolute deviation for all six fundamentals is 1.13 cm^{-1}. These data indicate that it is very difficult to go beyond wavenumber accuracy by a purely *ab initio* approach for molecules, such as H$_2$CS, in spite of a dedicated attempt to include the dominant HL corrections in a converged manner. This has also been noted in other cases.[37–42]

To put the present results into perspective, we compare the vibrational term values obtained with the present

TABLE IV. Best theoretical estimates of the vibrational wavenumbers of H$_2$CS (in cm^{-1}) compared with the available experimental data.

Mode	$\Gamma^{(C_{2v})}$	VQZ-F12*	VQZ-F12$^{*\mathrm{HL}}$	Exp.[10]	VQZ-F12*–Exp.	VQZ-F12$^{*\mathrm{HL}}$–Exp.
ν_1	A$_1$	2969.47	2972.46	2971.03	–1.56	1.43
ν_2	A$_1$	1454.50	1455.72	1455.50	–1.00	0.22
ν_3	A$_1$	1061.81	1060.61	1059.21	2.60	1.40
ν_4	B$_1$	990.59	990.63	990.18	0.41	0.45
ν_5	B$_2$	3024.32	3027.74	3024.62	–0.30	3.12
ν_6	B$_2$	989.59	990.85	991.02	–1.43	–0.17
2ν_2	A$_1$	2875.24	2877.80	2877.11	–1.87	0.69
$\nu_2 + \nu_3$	A$_1$	2511.92	2511.92	2511.60	0.32	0.32

TABLE V. Best theoretical estimates of the vibrational term values of H_2CS (in cm^{-1}) from the *ab initio* VQZ-F12 and VQZ-F12^{*HL} PESs (see text) compared with the results obtained using the refined PES of Carter and Handy (Ref. 23).

Mode	$\Gamma^{(C_{2v})}$	VQZ-F12	VQZ-F12^{*HL}	Carter	VQZ-F12–Carter	VQZ-F12^{*HL}–Carter
ν_6	B_2	990.09	990.85	990.88	–0.79	–0.03
ν_4	B_1	991.02	990.63	990.55	0.47	0.08
ν_3	A_1	1062.11	1060.61	1058.86	3.25	1.75
ν_2	A_1	1455.27	1455.72	1457.34	–2.07	–1.62
$2\nu_6$	A_1	1966.52	1966.96	1978.70	–12.18	–11.74
$\nu_4 + \nu_6$	A_2	1989.36	1989.68	2009.26	–19.90	–19.58
$2\nu_4$	A_1	1992.66	1992.86	1939.58	53.08	53.28
$\nu_3 + \nu_4$	B_1	2048.06	2046.67	2045.00	3.06	1.67
$\nu_3 + \nu_6$	B_2	2048.65	2047.32	2045.49	3.16	1.83
$2\nu_3$	A_1	2114.55	2111.53	2101.79	12.76	9.74
$\nu_2 + \nu_6$	B_2	2430.22	2431.38	2430.56	–0.34	0.82
$\nu_2 + \nu_4$	B_1	2440.04	2439.96	2484.39	–44.35	–44.43
$\nu_2 + \nu_3$	A_1	2512.97	2511.92	2510.68	2.29	1.24
$2\nu_2$	A_1	2876.46	2877.80	2875.77	0.69	2.03
$3\nu_6$	B_2	2948.41	2949.98	2956.84	–8.43	–6.86
$3\nu_4$	B_1	2956.09	2955.54	2863.36	92.73	92.18
ν_1	A_1	2970.18	2972.46	2969.90	0.28	2.56
$2\nu_4 + \nu_6$	B_2	2999.32	2999.89	2981.01	18.31	18.88
$2\nu_6 + \nu_4$	B_1	3001.52	3001.76	3024.75	–23.23	–22.99
$2\nu_6 + \nu_3$	A_1	3020.21	3019.03	3028.99	–8.78	–9.96
ν_5	B_2	3024.68	3027.74	3024.50	0.18	3.24
$\nu_3 + \nu_4 + \nu_6$	A_2	3042.82	3041.54	3059.33	–16.51	–17.79
$2\nu_4 + \nu_3$	A_1	3046.15	3044.76	2991.83	54.32	52.93
$2\nu_3 + \nu_4$	B_1	3096.49	3094.11	3083.10	13.39	11.01
$2\nu_3 + \nu_6$	B_2	3096.53	3093.06	3084.18	12.35	8.88
$3\nu_3$	A_1	3157.26	3152.76	3128.33	28.93	24.43
$2\nu_6 + \nu_2$	A_1	3395.35	3396.72	3399.95	–4.60	–3.23
$\nu_2 + \nu_4 + \nu_6$	A_2	3424.14	3424.77	3491.53	–67.39	–66.76
$2\nu_4 + \nu_2$	A_1	3431.19	3431.03	3460.53	–29.34	–29.50
$\nu_2 + \nu_3 + \nu_6$	B_2	3484.15	3483.74	3480.46	3.69	3.28
$\nu_2 + \nu_3 + \nu_4$	B_1	3493.08	3491.42	3533.13	–40.05	–41.71
$2\nu_3 + \nu_2$	A_1	3561.03	3558.44	3548.11	12.92	10.33
$2\nu_2 + \nu_6$	B_2	3841.53	3843.39	3838.53	3.00	4.86
$2\nu_2 + \nu_4$	B_1	3857.36	3858.07	4009.80	–152.44	–151.73
$2\nu_2 + \nu_3$	A_1	3932.31	3932.06	3926.66	5.65	5.40
$3\nu_2$	A_1	4285.33	4287.20	4283.67	1.66	3.53

ab initio PESs to those obtained with the refined PES of Carter and Handy[23] (Table V). Since the VQZ-F12* results have already been presented in Table III, we employ the VQZ-F12 and VQZ-F12^{*HL} results for these comparisons. All three surfaces considered perform equally well for the fundamental term values, but the results from the previous PES (Ref. 23) start to deviate greatly already for the first overtones, with a maximum deviation of 53 cm^{-1} for $2\nu_4$, and even more so for the higher combination bands with a maximum deviation of 152 cm^{-1} for $2\nu_2 + \nu_4$. Since the present PESs are fully *ab initio*, we expect them to be more reliable in terms of predicting energies for higher excitations. By contrast, the previously refined PES (Ref. 23) was obtained by fitting a quartic force field to the rotational, fundamental, $2\nu_2$, and $\nu_2 + \nu_3$ bands of H_2CS, and it thus seems likely that this PES will not guarantee high accuracy beyond this training set of states: judging from the present comparisons, it appears to have deficiencies in the description of C–S stretching and out-of-plane bending motions.

IV. CONCLUSIONS

In this work, we present two *ab initio* potential energy surfaces for the ground electronic state of H_2CS. They have been calculated purely *ab initio* in an attempt of pushing the accuracy towards the currently feasible limit. The first surface is generated at the VQZ-F12* level (i.e., CCSD(T) near the CBS limit), while the second one incorporates additive high-level corrections for core-valence correlation, higher order correlation effects beyond CCSD(T), and relativistic effects as well as diagonal Born-Oppenheimer corrections (without nonadiabatic terms). Special care has been taken to obtain converged values for all these terms. Both surfaces provide vibrational term values close to wavenumber accuracy (Table IV). The two sets of variationally calculated results are similar because the effects of the different high-level corrections compensate each other to a large extent and in an apparently systematic manner. In particular, the large positive shifts in the computed wavenumbers caused by the core-valence correlation terms (up to $+15\ \mathrm{cm}^{-1}$) are counteracted by similarly large negative shifts from the higher order correlation terms (up to $-14\ \mathrm{cm}^{-1}$).

On the basis of the current results, we believe that it is difficult to go beyond wavenumber accuracy in a purely *ab initio* fashion for a molecule such as H_2CS. In the future, we therefore plan to perform an empirical optimization of the current *ab initio* surfaces by a slight adjustment through least-squares fittings to the few accurate experimental energies of H_2CS that are available. Such a refined surface should allow us to approach experimental accuracy in simulations of rotational-vibrational spectra, provided that we apply the same type of approximate TROVE procedure as during the least-squares refinement.[75] We believe that each of our current *ab initio* surfaces can be used successfully as initial guess for the refinement process: their documented accuracy is essential for this purpose, since the amount of available experimental data is very limited in the case of H_2CS.

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