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A new "spectroscopic" potential energy surface for formaldehyde in its ground electronic state

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We report a new "spectroscopic" potential energy surface (PES) of formaldehyde ($H_2{}^{12}C^{16}O$) in its ground electronic state, obtained by refining an *ab initio* PES in a least-squares fitting to the experimental spectroscopic data for formaldehyde currently available in the literature. The *ab initio* PES was computed using the CCSD(T)/aug-cc-pVQZ method at 30 840 geometries that cover the energy range up to 44 000 cm^{-1} above equilibrium. Ro-vibrational energies of formaldehyde were determined variationally for this *ab initio* PES by means of the program TROVE [Theoretical ROtation-Vibration Energies; S. N. Yurchenko, W. Thiel, and P. Jensen, J. Mol. Spectrosc. **245**, 126 (2007)]. The parameter values in the analytical representation of the PES were optimized in fittings to 319 ro-vibrational energies with $J = 0, 1, 2$, and 5. The initial parameter values in the fittings were those of the *ab initio* PES, the ro-vibrational eigenfunctions obtained from this PES served as a basis set during the fitting process, and constraints were imposed to ensure that the refined PES does not deviate unphysically from the *ab initio* one in regions of configuration space not sampled by the experimental data. The resulting refined PES, referred to as H_2CO-2011, reproduces the available experimental $J \leq 5$ data with a root-mean-square error of 0.04 cm^{-1}. *© 2011 American Institute of Physics*. [doi:10.1063/1.3599927]

I. INTRODUCTION

An important goal of theoretical spectroscopy is the generation of accurate ground-state potential energy surfaces (PESs) for small polyatomic molecules. The PESs obtained are intended to serve as input for variational computations of highly accurate ro-vibrational term values with deviations from experiment typically below 0.1 cm^{-1}. In order to achieve this accuracy, an "empirical" approach is required in which an *ab initio* PES is refined in least-squares fittings to experimentally derived energies or observed wavenumbers. The PESs determined in this manner are generally referred to as "spectroscopic" potentials. The semi-empirical PESs of H_3^+, H_2O, H_2Te, H_2S, O_3, CO_2, and NH_3 (Refs. 1–8) are successful examples of this strategy being employed towards approaching spectroscopic accuracy in the theoretical calculation of rotation-vibration energy levels.

Recently, we have implemented a new procedure[9] in the program suite TROVE (Ref. 10) for the refinement of an *ab initio* PES of a polyatomic molecule through least-squares fitting to experimental ro-vibrational energies. We have already applied this approach to construct "spectroscopic" PESs for $^{121}SbH_3$ and $^{14}NH_3$.[9,11] In the present work, we generate an accurate "spectroscopic" PES for $H_2{}^{12}C^{16}O$ (henceforth referred to as formaldehyde or H_2CO). We first compute a six-dimensional *ab initio* PES for ground-state H_2CO by means of standard coupled cluster theory CCSD(T)[12–14] in conjunction with the augmented correlation-consistent atomic basis set aug-cc-pVQZ.[15,16] When we use this *ab initio* PES for variational TROVE (Ref. 10) calculations of the vibrational energies, the resulting energies typically deviate from the experimentally derived values by up to several reciprocal cm. As we are aiming for a "spectroscopic accuracy" of better than 0.1 cm^{-1}, we refine the *ab initio* PES in a least-squares fitting to the available experimental ro-vibrational energies for $J = 0, 1, 2$, and 5. The resulting "spectroscopic" PES reproduces the experimentally determined term values of formaldehyde for $J \leq 5$ with a root-mean-square (rms) error of 0.04 cm^{-1}.

The spectrum of H_2CO is important in diverse applications, including atmospheric, interstellar, and combustion chemistry. A number of *ab initio* PESs for H_2CO, computed at various levels of theory, are available. Martin *et al.*[17] determined the *ab initio* quartic force field using the CCSD(T)/cc-pVTZ and CCSD(T)/cc-pVQZ methods and reported theoretical values for structural and spectroscopic parameters. A set of multiresolution PESs were recently computed by Yagi *et al.*[18] by combining B3LYP/cc-pVDZ, CCSD/cc-pVDZ, and CCSD(T)/cc-pVTZ results. Global ground-state PESs were constructed for formaldehyde by Jalbout and Chang[19] on the basis of combined *ab initio* and DFT results and by Zhang *et al.*[20] in purely *ab initio* calculations at the CCSD(T)/aug-cc-pVTZ and MR-CI/aug-cc-pVTZ levels of theory.

No available theoretical PES of H_2CO is capable of providing the accuracy that we target in the present work. An empirical adjustment of the force field from Ref. 17, aimed at improving the agreement with experimentally derived vibrational energies, was made by Carter *et al.*[21] The rms deviation attained was 1.1 cm^{-1}. In Ref. 22, Carter *et al.* improved their

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PES by including the term values of rotationally excited states with $J \leq 3$ (measured relative to the $J = 0$ level of the vibrational state in question) of H_2CO and D_2CO in the refinement. For these term values, the rms deviations were 0.002 cm^{-1} ($J = 1$), 0.005 cm^{-1} ($J = 2$), and 0.009 cm^{-1} ($J = 3$) for the ground and fundamental vibrational states, and 1.1 cm^{-1} for all $J = 0$ vibrational term values (measured relative to the $J = 0$ level of the vibrational ground state) below 4000 cm^{-1}. Burleigh *et al.*[23] obtained a "spectroscopic" force field by refining the force constants from Ref. 17 in the fittings (with a rms deviation of 1.5 cm^{-1}) to the vibrational band centers from Ref. 24. Similar fittings have been carried out by Mardis and Sibert[25] (rms deviation: 1.5 cm^{-1} for 139 term values) and by Bernal and Lemus[26] (rms deviation: 2.39 cm^{-1} for 260 states) who employed an algebraic local-mode model for the vibrational motion. Bekhtereva[27] and Ulenikov *et al.*[28] generated empirically adjusted force constant values in global fittings to the vibrational band centers of H_2CO, HDCO, and D_2CO (rms deviation: 0.97 cm^{-1} for 254 levels).

A detailed review of the experimentally available spectroscopic data for H_2CO is given in Ref. 29. In the PES fittings of the present work, input data derived from the following vibrational transitions have been employed: The 5.7 μm and 3.6 μm band systems[30]; the 3.5 μm band system[31]; the hot transitions $\nu_4 - \nu_4$, $\nu_1 + \nu_4 - \nu_4$, $\nu_4 + \nu_5 - \nu_4$ (Ref. 32); and the band centers reported in Refs. 24, 31, 33, and 34. The band centers obtained from the dispersed fluorescence spectra[24] are of special importance in the present work. Despite their relatively low resolution, these data are associated with an extensive set of vibrationally excited states. Thus, they sample large portions of vibrational configuration space and are essential for the accurate determination of the PES at high energies. In the PES refinement of the present work, we did not use as input the H_2CO data compiled in the databases HITRAN (Ref. 35) and GEISA (Ref. 36) because of the well-documented deficiencies of these data (see, for example, the discussion in Ref. 29).

The paper is structured as follows. The *ab initio* calculations and the analytical representation of the PES are described in Sec. II. The computational procedure is outlined in Sec. III. The selection of the experimental data for the refinement is discussed in Sec. IV. The results of the refinement are presented in Sec. V which also offers conclusions.

II. THE *AB INITIO* POTENTIAL ENERGY SURFACE

The six-dimensional *ab initio* PES of H_2CO was computed at 30 840 geometries with energies ranging up to 44 000 cm^{-1} above equilibrium. The quantum-chemical calculations were done at the CCSD(T) (coupled cluster theory involving single and double excitations, with a quasi-perturbative treatment of triple excitations[12–14]) level of theory using the frozen-core approximation and the augmented correlation-consistent aug-cc-pVQZ basis.[15,16] The CCSD(T) calculations were performed with the MOLPRO 2006 package[37,38] using the default thresholds. The equilibrium structural parameters of H_2CO obtained from the *ab initio* results are listed in Table I, where they are compared with the experimentally derived and theoretical literature values.

TABLE I. Equilibrium structures of H_2CO (bond lengths are in Å and angles in degrees).

Method	r^{e}_{CO}	r^{e}_{CH}	θ^{e}_{OCH}	Reference
CCSD(T)/aug-cc-pVQZ	1.20754	1.10222	121.693	This work
Refined PES-2011	1.20367	1.10290	121.781	This work
CCSD(T)/cc-pVQZ	1.2066	1.1022	121.78	17
CCSD(T)/cc-pVTZ	1.2115	1.1031	121.7	20
Refined	1.20312 (50)	1.10034(50)	121.62(5)	39
Refined	1.20296	1.10064	121.648	22
Experimentally derived	1.2033(10)	1.1005(20)	121.91(15)	40

In order to represent analytically the *ab initio* PES, we employ a Taylor-like expansion around the minimum energy path (MEP) for out-of-plane motion

$$\begin{aligned} V(r_1, r_2, r_3, \theta_1, \theta_2, \tau) &= \sum_{ijklmn} f_{ijklmn} (1 - e^{-\Delta r_1})^i (1 - e^{-\Delta r_2})^j \\ &\quad (1 - e^{-\Delta r_3})^k (\Delta\theta_1)^l (\Delta\theta_2)^m (\cos\tau + 1)^n, \end{aligned} \tag{1}$$

with the maximum expansion order $i + j + k + l + m + n = 6$.

In Eq. (1), we use the three stretching coordinates

$$\Delta r_1 = r_{CO} - r^{\rm ref}_{CO}(\tau), \tag{2}$$

$$\Delta r_2 = r_{CH_1} - r^{\rm ref}_{CH}(\tau), \tag{3}$$

$$\Delta r_3 = r_{CH_2} - r^{\rm ref}_{CH}(\tau), \tag{4}$$

the two bending coordinates

$$\Delta\theta_1 = \theta_{OCH_1} - \theta^{\rm ref}_{OCH}(\tau), \tag{5}$$

$$\Delta\theta_2 = \theta_{OCH_2} - \theta^{\rm ref}_{OCH}(\tau), \tag{6}$$

and the out-of-plane bending coordinate τ. Here, r_{CO}, r_{CH_1}, and r_{CH_2} are the bond lengths, θ_{OCH_1} and θ_{OCH_2} are the bond

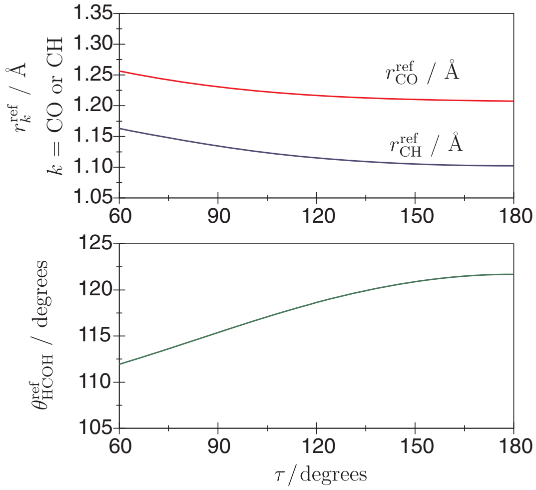

FIG. 1. Variation of the reference bond length values $r^{\rm ref}_{CO}$ and $r^{\rm ref}_{CH}$ (top panel) and of the reference bond angle value $\theta^{\rm ref}_{OCH}$ (bottom panel) along the minimum energy path (see text) of H_2CO.

angles, and τ is the dihedral angle between the OCH_1 and OCH_2 planes. The sign of τ is chosen such that an observer on the O nucleus, who is looking towards the C nucleus, will see the rotation by τ from the CH_1 bond to the CH_2 bond as an anti-clockwise rotation.

Formaldehyde has the molecular symmetry (MS) group $\boldsymbol{C}_{2\mathrm{v}}(\mathrm{M})$,[41] and so the potential function of H_2CO is invariant to the interchange to the two protons. This imposes the condition $f_{i(jk)(lm)n} = f_{i(kj)(ml)n}$ for the expansion coefficients in Eq. (1). The coordinates $r_{\mathrm{CO}}, r_{\mathrm{CH}_1}, r_{\mathrm{CH}_2}, \theta_{\mathrm{OCH}_1},$ and θ_{OCH_2} are all invariant under the spatial inversion operator E^*,[41] while $E^*\tau = 360^\circ - \tau$. However, E^* $\cos\tau = \cos\tau$ and the expression for V in Eq. (1) is invariant under E^* as required by symmetry. When the molecule is planar, $\tau = 180^\circ$, and the quantity $(\cos\tau + 1)$ in Eq. (1) vanishes. The reference structural parameters $r^{\mathrm{ref}}_{\mathrm{CO}}(\tau)$, $r^{\mathrm{ref}}_{\mathrm{CH}}(\tau)$, and $\theta^{\mathrm{ref}}_{\mathrm{OCH}}(\tau)$ defining the MEP of H_2CO were determined *ab initio* at the CCSD(T)/aug-cc-pVQZ level in geometry optimizations at 10 values of τ equidistantly distributed between $\tau = 80^\circ$ and $\tau = 180^\circ$. They were then expanded in terms of $(\cos\tau + 1)$ as follows:

$$r^{\mathrm{ref}}_{\mathrm{CO}}(\tau) = \sum_{n=0}^{4} a_n^{\mathrm{CO}}(\cos\tau + 1)^n, \tag{7}$$

$$r^{\mathrm{ref}}_{\mathrm{CH}}(\tau) = \sum_{n=0}^{3} a_n^{\mathrm{CH}}(\cos\tau + 1)^n, \tag{8}$$

$$\theta^{\mathrm{ref}}_{\mathrm{OCH}}(\tau) = \sum_{n=0}^{2} a_n^{\mathrm{OCH}}(\cos\tau + 1)^n. \tag{9}$$

The computed MEP is shown in Fig. 1. The expansion parameters a_n^{X} (X=CO, CH, and OCH), obtained in separate fittings to the 10 chosen data points are listed in Table II; the rms deviations of these fittings are 10^{-5} Å, 2×10^{-6} Å, and 3×10^{-5} rad for the CO, CH, and OCH parameters, respectively. The global minimum is found at $r^{\mathrm{e}}_{\mathrm{CO}} = 1.20754$ Å, $r^{\mathrm{e}}_{\mathrm{CH}} = 1.10222$ Å, and $\theta^{\mathrm{e}}_{\mathrm{OCH}} = 121.693^\circ$. These values are in keeping with the equilibrium parameters from the literature (see Table I).

With the MEP defined by Eqs. (7)–(9) in conjunction with Table II, we have determined the remaining potential parameter values in a least-squares fitting to the complete set of computed *ab initio* energies. In this fitting, we could usefully vary 110 parameters f_{ijklmn} in Eq. (1) to get an overall root-mean-square error of 1.05 cm^{-1} (0.56 cm^{-1} for the points with energies below 5000 cm^{-1}). We used weight factors of the form suggested by Partridge and Schwenke[42]

$$w_i = \frac{\tanh[-0.0006\ \mathrm{cm} \times (V_i - 16\,000\ \mathrm{cm}^{-1})] + a}{b \times V_i^{(w)}}, \tag{10}$$

where $a = 1.002002002$, $b = 2.002002002$ cm, $V_i^{(w)} = \max(16\,000\ \mathrm{cm}^{-1}, V_i)$, and V_i is the *ab initio* energy at the ith geometry (in cm^{-1}) measured relative to the equilibrium energy. The *ab initio* energy V_i is weighted by the factor w_i in the PES fitting; these weight factors favor the energies below 16 000 cm^{-1}. The *ab initio* values of the parameters f_{ijklmn} are given in the supplementary material to the present paper.[43] The analytical representation of the H_2CO PES [Eq. (1)] corresponding to these parameter values will be referred to as AVQZ as this reflects the underlying level of *ab initio* theory, CCSD(T)/aug-cc-pVQZ.

TABLE II. Expansion parameters a_n^{X} (X = CO, CH, and OCH) defining the reference structure of H_2CO (bond lengths are in Å, angles in radian).

	CO	CH	OCH
a_0	1.2075443	1.10221709	2.123948763
a_1	0.0162744135	0.0208797432	− 0.103629709
a_2	0.0059211995	0.0079106055	− 0.0066300781
a_3	− 0.0041248571	0.0034126562	
a_4	0.0049473990		

To assess the quality of the AVQZ PES of H_2CO, we have calculated a set of vibrational band centers associated with it by means of the TROVE approach[10] (see Sec. III for the computational details). Tables III–VI include the calculated band center values (relative to the calculated zero point energy of 5769.78 cm^{-1}) and compare them with the available experimental values from the literature (see Sec. IV for the corresponding references). The rms deviation between theory and experiment is 5.1 cm^{-1} for all term values below 7200 cm^{-1}. The fundamental term values are accurate to better than 1.4 cm^{-1}, except for the asymmetric bending mode ν_6 for which the fundamental term value deviates by 3.5 cm^{-1} from experiment. In view of the fact that at the CCSD(T)/aug-cc-pVQZ level of *ab initio* theory, we neglect, for example, higher-order coupled cluster excitations, core-valence correlation, basis set incompleteness, and relativistic effects, the agreement with experiment achieved with the AVQZ PES is better than expected. We also note that the purely rotational term values for $J \leq 5$ (see Table VII below) are reproduced very well, with an rms error of 0.094 cm^{-1}. This indicates that the AVQZ equilibrium geometry is quite accurate. In summary, the new AVQZ PES of H_2CO appears to be of high quality and should, thus, provide a good starting point for refinement of the PES in least-squares fittings to the experimental data.

III. TROVE: COMPUTATIONAL DETAILS

We compute the ro-vibrational energies of H_2CO by means of the variational program suite TROVE.[10] In the variational calculations, we generate the matrix representation of the rotation-vibration Hamiltonian in terms of a symmetry-adapted basis set constructed as follows: The primitive vibrational basis functions are given by the products of one-dimensional (1D) vibrational functions $\phi_{n_1}(r_1^\ell)$, $\phi_{n_2}(r_2^\ell)$, $\phi_{n_3}(r_3^\ell)$, $\phi_{n_4}(\theta_1^\ell)$, $\phi_{n_5}(\theta_2^\ell)$, and $\phi_{n_6}(\tau)$. Here, $(r_1^\ell, r_2^\ell, r_3^\ell, \theta_1^\ell, \theta_2^\ell)$ are linearized versions[10,41] of the coordinates $r_{\mathrm{CO}}, r_{\mathrm{CH}_1}, r_{\mathrm{CH}_2}, \theta_{\mathrm{OCH}_1}$, and θ_{OCH_2}, respectively. We use the Numerov-Cooley technique[44,45] to determine the functions $\phi_{n_i}(q_i)$ (where n_i denotes the principal quantum number) by solving the 1D Schrödinger equation[10] for the vibrational motion associated with the corresponding coordinate q_i

TABLE III. Residuals (Obs.−Calc.; in cm^{-1}) for selected $J = 0$, $\Gamma = A_1$ energy levels of H_2CO, computed with TROVE from the *ab initio* AVQZ (A) and refined H_2CO-2011 (R) PESs. The "observed" values are from Ref. 24, unless indicated.

State	Obs.	Calc. (A)	Obs.–(A)	Calc.(R)	Obs.–(R)
ν_3	1500.1747[a]	1499.10	1.07	1500.19	−0.01
ν_2	1746.0093[b]	1744.61	1.40	1746.03	−0.02
$2\nu_4$	2327.5239[b]	2325.18	2.35	2327.54	−0.01
$\nu_3+\nu_6$	2494.3543[b]	2487.73	6.63	2494.34	0.01
ν_1	2782.4575[b]	2781.74	0.71	2782.46	0.00
$\nu_3+\nu_6$	2998.9873[b]	2997.24	1.74	2998.94	0.04
$\nu_2+\nu_3$	3238.4548[b]	3236.11	2.35	3238.36	0.09
$2\nu_2$	3471.6	3469.39	2.21	3471.23	0.37
$\nu_3+2\nu_4$	3825.3	3822.43	2.87	3825.94	−0.64
$3\nu_6$	3937.4	3929.86	7.54	3936.02	1.38
$\nu_2+2\nu_4$	4058.3	4054.60	3.70	4058.53	−0.23
$\nu_5+\nu_6$	4083.1	4078.88	4.22	4083.21	−0.11
$\nu_2+\nu_3+\nu_6$	4248.7	4241.02	7.68	4247.13	1.57
$\nu_1+\nu_3$	4253.8	4253.86	−0.06	4254.58	−0.78
$\nu_1+\nu_2$	4529.5025[c]	4527.54	1.96	4529.82	−0.31
$4\nu_4$	4629.0	4625.12	3.88	4628.59	0.41
$\nu_2+\nu_3+\nu_6$	4730.8	4726.16	4.64	4732.59	−1.79
$\nu_3+2\nu_4+\nu_6$	4842.0	4834.67	7.33	4840.93	1.07
$2\nu_2+\nu_3$	4955.2	4952.81	2.39	4954.65	0.55
$\nu_1+2\nu_4$	5092.4	5089.97	2.43	5092.32	0.08
$3\nu_2$	5177.7595[c]	5175.01	2.75	5177.82	−0.06
$\nu_3+2\nu_4+\nu_6$	5325.6	5317.59	8.01	5324.51	1.09
$4\nu_6$	5389.4	5380.66	8.74	5386.16	3.24
$2\nu_1$	5462.7	5460.43	2.27	5462.94	−0.24
$\nu_2+\nu_3+2\nu_4$	5546.5	5540.40	6.10	5545.43	1.07
$\nu_2+\nu_3+2\nu_4$	5551.3	5548.73	2.57	5553.13	−1.83
$\nu_1+\nu_5$	5651.1904[d]	5650.04	1.15	5651.38	−0.19
$\nu_2+3\nu_6$	5687.9	5681.97	5.93	5688.20	−0.30
$\nu_1+\nu_3+\nu_6$	5729.2	5727.84	1.36	5729.86	−0.66
$2\nu_2+\nu_3+\nu_6$	5809.5	5804.16	5.34	5810.02	−0.52
$2\nu_3+2\nu_6$	5986.2	5985.47	0.73	5984.48	1.72
$\nu_3+4\nu_4$	6123.6	6119.14	4.46	6123.36	0.24
$\nu_1+2\nu_2$	6254.7	6252.59	2.11	6253.93	0.77
$2\nu_4+3\nu_6$	6263.1	6258.82	4.28	6262.05	1.05
$4\nu_3+\nu_6$	6373.4	6357.54	15.86	6372.06	1.34
$2\nu_4+\nu_5+\nu_6$	6401.2	6395.01	6.19	6399.83	1.37
$2\nu_2+\nu_3+\nu_6$	6447.6	6434.19	13.41	6445.83	1.77
$\nu_2+2\nu_3+2\nu_6$	6553.1	6540.24	12.86	6550.09	3.01
$\nu_1+\nu_3+2\nu_4$	6562.7	6561.59	1.11	6565.39	−2.69
$\nu_2+\nu_3+2\nu_4+\nu_6$	6578.8	6570.97	7.83	6575.74	3.06
$2\nu_5+\nu_6$	6635.7	6627.25	8.45	6633.85	1.85
$3\nu_2+\nu_3$	6652.2	6649.83	2.37	6655.34	−3.14
$2\nu_5+\nu_6$	6777.6	6764.53	13.07	6772.28	5.32
$2\nu_3+2\nu_4+\nu_6$	6815.2	6809.16	6.04	6816.11	−0.91
$\nu_1+\nu_2+2\nu_4$	6825.5	6821.88	3.62	6823.88	1.62
$6\nu_4$	6910.7	6903.18	7.52	6910.15	0.55
$2\nu_1+\nu_3$	6921.3	6913.39	7.91	6919.35	1.95
$\nu_2+2\nu_3+\nu_5$	7137.4	7139.51	−2.11	7140.25	−2.85

[a] Reference 30;
[b] Reference 31;
[c] Reference 33;
[d] Reference 34.

TABLE IV. Residuals (Obs.−Calc.; in cm^{-1}) for selected $J = 0$, $\Gamma = A_2$ energy levels of H_2CO, computed with TROVE from the *ab initio* AVQZ (A) and refined H_2CO-2011 (R) PESs. The "observed" values are from Ref. 24 unless indicated.

State	Obs.	Calc. (A)	Obs.–(A)	Calc.(R)	Obs.–(R)
$\nu_4+\nu_6$	2422.9701[a]	2418.43	4.54	2422.69	0.28
$2\nu_3+\nu_4$	3886.5	3883.37	3.13	3886.47	0.03
$\nu_4+\nu_5$	3996.5180[b]	3994.75	1.77	3996.54	−0.03
$\nu_2+\nu_4+\nu_6$	4163.2890[c]	4159.35	3.94	4164.12	−0.83
$3\nu_4+\nu_6$	4741.9	4736.21	5.69	4742.10	−0.20
$3\nu_3+\nu_4$	5353.2	5354.69	−1.49	5356.66	−3.46
$\nu_2+2\nu_3+\nu_4$	5625.5	5621.51	3.99	5624.72	0.78
$\nu_2+\nu_4+\nu_5$	5717.7	5715.14	2.56	5718.18	−0.48
$2\nu_2+\nu_4+\nu_6$	5887.5	5883.43	4.07	5888.43	−0.93
$2\nu_3+3\nu_4$	6189.1	6184.41	4.69	6190.55	−1.45
$3\nu_4+\nu_5$	6281.9	6279.00	2.90	6281.68	0.22
$\nu_2+3\nu_4+\nu_6$	6465.2	6458.94	6.26	6464.58	0.62
$\nu_3+\nu_4+\nu_5+\nu_6$	6492.1	6487.90	4.20	6491.50	0.60
$5\nu_4+\nu_6$	7030.7	7027.00	3.70	7032.38	−1.68
$\nu_2+3\nu_3+\nu_4$	7088.6	7089.26	−0.66	7094.70	−6.10

[a] Reference 31.
[b] Reference 32.
[c] Reference 33.

TABLE V. Residuals (Obs.−Calc.; in cm^{-1}) for selected $J = 0$, $\Gamma = B_1$ energy levels of H_2CO computed with TROVE from the *ab initio* AVQZ (A) and refined H_2CO-2011 (R) PESs. The "observed" values are from Ref. 24 unless indicated.

State	Obs.	Calc. (A)	Obs.–(A)	Calc.(R)	Obs.–(R)
ν_4	1167.2563[a]	1166.10	1.16	1167.30	−0.05
$\nu_3+\nu_4$	2667.0481[b]	2664.64	2.40	2667.03	0.02
$\nu_2+\nu_4$	2905.9685[b]	2903.35	2.61	2905.97	−0.01
$3\nu_4$	3480.7	3478.04	2.66	3481.03	−0.33
$\nu_3+\nu_4+\nu_6$	3673.5	3668.88	4.62	3675.07	−1.57
$\nu_1+\nu_4$	3941.5295[c]	3939.85	1.68	3941.52	0.01
$\nu_2+\nu_3+\nu_4$	4397.5	4394.05	3.45	4397.14	0.36
$2\nu_2+\nu_4$	4624.3	4620.66	3.64	4623.37	0.93
$\nu_3+3\nu_4$	4977.1	4973.76	3.34	4977.71	−0.61
$\nu_4+3\nu_6$	5104.0	5104.08	−0.08	5106.65	−2.65
$\nu_2+3\nu_4$	5205.2	5200.75	4.45	5205.09	0.11
$\nu_4+\nu_5+\nu_6$	5244.1	5241.90	2.20	5245.34	−1.24
$\nu_2+\nu_3+\nu_4+\nu_6$	5417.6	5413.05	4.55	5417.35	0.25
$\nu_1+\nu_2+\nu_4$	5680.0	5678.47	1.53	5681.15	−1.15
$5\nu_4$	5771.0	5766.75	4.25	5771.29	−0.29
$\nu_3+3\nu_4+\nu_6$	5996.0	5992.36	3.64	5997.11	−1.11
$2\nu_2+\nu_3+\nu_4$	6106.2	6103.05	3.15	6106.04	0.16
$\nu_1+3\nu_4$	6235.2	6233.21	1.99	6235.44	−0.24
$3\nu_2+\nu_4$	6321.7	6318.68	3.02	6322.30	−0.60
$2\nu_3+\nu_4+\nu_5$	6553.3	6548.32	4.98	6549.82	3.48
$2\nu_1+\nu_4$	6611.6	6609.33	2.27	6611.27	0.33
$\nu_2+\nu_3+3\nu_4$	6693.4	6687.87	5.53	6693.34	0.06
$\nu_1+\nu_4+\nu_5$	6710.0	6704.34	5.66	6708.68	1.32
$\nu_1+\nu_4+\nu_5$	6795.1	6793.70	1.40	6794.14	0.96
$\nu_2+\nu_4+3\nu_6$	6849.7	6844.88	4.82	6848.88	0.82
$\nu_1+\nu_3+\nu_4+\nu_6$	6894.6	6886.29	8.31	6892.96	1.64
$2\nu_2+\nu_3+\nu_4+\nu_6$	6964.1	6960.35	3.75	6965.32	−1.22

[a] Reference 30.
[b] Reference 31.
[c] Reference 32.

TABLE VI. Residuals (Obs.−Calc.; in cm^{-1}) for selected $J = 0$, $\Gamma = B_2$ energy levels of H_2CO, computed with TROVE from the *ab initio* AVQZ (A) and refined H_2CO-2011 (R) PESs. The "observed" values are from Ref. 24 unless indicated.

State	Obs.	Calc. (A)	Obs.-(A)	Calc.(R)	Obs.-(R)
ν_6	1249.0948[a]	1245.60	3.49	1249.07	0.03
$2\nu_3$	2719.1550[b]	2715.24	3.92	2719.15	0.01
ν_5	2843.3256[b]	2842.37	0.95	2843.31	0.01
$\nu_2+\nu_6$	3000.0659[b]	2995.91	4.16	3000.08	− 0.01
$2\nu_4+\nu_6$	3586.6	3581.09	5.51	3586.55	0.05
$\nu_1+\nu_6$	4021.0807[c]	4017.70	3.38	4021.26	− 0.18
$3\nu_3$	4192.3816[c]	4189.62	2.77	4192.62	− 0.24
$\nu_3+\nu_5$	4335.0971[c]	4334.78	0.32	4334.97	0.13
$\nu_2+2\nu_3$	4466.8	4462.47	4.33	4466.04	0.76
$\nu_2+\nu_5$	4571.6947[c]	4568.46	3.24	4571.31	0.39
$2\nu_2+\nu_6$	4734.2078[c]	4729.81	4.40	4734.27	− 0.07
$2\nu_3+2\nu_4$	5043.7	5038.23	5.47	5042.49	1.21
$2\nu_4+\nu_5$	5140.1	5137.18	2.92	5141.13	− 1.03
$4\nu_3$	5151.0	5146.07	4.93	5154.61	− 3.61
$\nu_2+2\nu_4+\nu_6$	5312.2	5305.84	6.36	5313.16	− 0.96
$\nu_2+2\nu_4+\nu_6$	5321.3	5318.94	2.36	5324.12	− 2.82
$2\nu_5$	5433.4	5429.38	4.02	5433.41	− 0.01
$\nu_2+\nu_3+2\nu_6$	5489.0	5481.41	7.59	5490.40	− 1.40
$2\nu_5$	5530.5	5528.61	1.89	5532.12	− 1.62
$\nu_1+\nu_2+\nu_6$	5768.8	5761.24	7.56	5767.72	1.08
$4\nu_4+\nu_6$	5891.8	5884.64	7.16	5890.37	1.43
$\nu_2+\nu_3+\nu_5$	6051.7	6050.44	1.26	6053.30	− 1.60
$2\nu_2+2\nu_3$	6194.8	6192.16	2.64	6195.37	− 0.57
$2\nu_2+\nu_5$	6276.4	6271.20	5.20	6276.02	0.38
$\nu_1+2\nu_4+\nu_6$	6346.2	6335.45	10.75	6346.55	− 0.35
$3\nu_3+2\nu_4$	6508.8	6505.56	3.24	6509.15	− 0.35
$\nu_5+3\nu_6$	6582.3	6577.27	5.03	6586.45	− 4.15
$2\nu_1+\nu_6$	6683.7	6681.24	2.46	6686.22	− 2.52
$\nu_1+\nu_5+\nu_6$	6759.0	6755.25	3.75	6761.01	− 2.01
$\nu_2+2\nu_4+\nu_5$	6856.3	6852.22	4.08	6857.17	− 0.87
$\nu_3+2\nu_5$	6864.3	6863.15	1.15	6865.22	− 0.92
$\nu_2+4\nu_3$	6909.0	6900.39	8.61	6909.20	− 0.20

[a] Reference 30.
[b] Reference 31.
[c] Reference 33.

$\in \{r_1^\ell, r_2^\ell, r_3^\ell, \theta_1^\ell, \theta_2^\ell, \tau\}$, with the other coordinates held fixed at their equilibrium values.

The basis functions $\phi_{n_i}(q_i)$ are then utilized to solve variationally the $J = 0$ problem

$$\hat{H}_{\rm vib}|\Psi^{\Gamma}_{J=0,\gamma}\rangle = E^{\rm vib}_{\gamma}|\Psi^{\Gamma}_{J=0,\gamma}\rangle, \tag{11}$$

where $\hat{H}_{\rm vib}$ is the vibrational ($J = 0$) Hamiltonian

$$\hat{H}_{\rm vib} = \frac{1}{2}\sum_{\lambda\mu} p_\lambda G_{\lambda\mu} p_\mu + V + U. \tag{12}$$

Here, $E^{\rm vib}_{\gamma}$ and $\Psi^{\Gamma}_{J=0,\gamma}$ are the vibrational eigenvalues and eigenfunctions, respectively, and $\Gamma = A_1$, A_2, B_1, and B_2 are the irreducible representations of the $\boldsymbol{C}_{2v}$(M) molecular symmetry group[41] to which H_2CO belongs. In Eq. (12), p_λ and p_μ are generalized momenta conjugate to the coordinates q_λ and q_μ, respectively. The kinetic energy factors $G_{\lambda\mu}$ and the pseudo-potential U are represented as 8th-order expansions in the displacement coordinates $\Delta r_i^\ell = r_i^\ell - r_i^{\rm e}$ (i = 1, 2, 3) and $\Delta\theta_j^\ell = \theta_j^\ell - \theta^{\rm e}$ (j = 1, 2) with $r_i^{\rm e}$ and $\theta^{\rm e}$ representing the equilibrium bond lengths and bond angle of H_2CO in the ground electronic state. For consistency, the molecular potential energy function V in Eq. (1) is also expanded in terms of linearized coordinates $\{\xi_1^\ell, \xi_2^\ell, \xi_3^\ell, \theta_1^\ell, \theta_2^\ell\}$, where $\xi_i^\ell = 1 - \exp(-\Delta r_i^\ell)$; this expansion is also truncated after the 8th-order terms.

The pure vibrational eigenfunctions $\Psi^{\Gamma}_{J=0,\gamma}$ of the $J = 0$ Hamiltonian [Eq. (11)] are multiplied by the symmetrized symmetric-top rotational eigenfunction[10,46] $|J, K, m, \tau_{\rm rot}\rangle$ in order to generate the final symmetrized basis functions $\Psi^{\Gamma}_{J,K,\gamma}$. In terms of the quantum number $\tau_{\rm rot}$ (= 0 or 1), the rotational parity is defined as $(-1)^{\tau_{\rm rot}}$,[41] and $K = |k|$ with k and m (where $-J \le k, m \le J$) specifying the projections, in units of $\hbar$, of the rotational angular momentum onto the molecule-fixed z axis and the space-fixed Z-axis, respectively.[41] In this so-called ($J = 0$)-contracted basis set[47] of products $\Psi^{\Gamma}_{J=0,\gamma}|J, K, m, \tau_{\rm rot}\rangle$, the vibrational part $\hat{H}_{\rm vib}$ of the total Hamiltonian is diagonal with diagonal matrix elements given by eigenvalues $E^{\rm vib}_{\gamma}$.

In TROVE calculations, the size of the basis set, and therefore the size of the Hamiltonian matrix blocks, can be controlled by the polyad number P, which in the present case is given by

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

where the local-mode quantum numbers n_i are defined in connection with the primitive basis functions ϕ_{n_i}. Hence, we can choose a maximum value $P_{\rm max}$ of the polyad quantum number and then include in the primitive basis set only those combinations of ϕ_{n_i} for which $P \le P_{\rm max}$. In the present work we use $P_{\rm max} = 14$. The largest rotation-vibration matrix blocks that had to be diagonalized for H_2CO ($J = 5$) had dimensions of about 21 000. Routines from the LAPACK and ARPACK[48] libraries were employed for the diagonalizations.

The TROVE program automatically labels the eigenvalues and eigenvectors with quantum numbers, based on an analysis of which basis functions contribute most to the corresponding eigenfunctions. As explained above, the basis functions are in turn associated with the quantum numbers K, $\tau_{\rm rot}$, $\Gamma_{\rm vib}$, n_1, n_2, n_3, n_4, n_5, and n_6. Here n_1, n_2, n_3 are stretching local mode quantum numbers,[49] describing the C–O, C–H$_1$, and C–H$_2$ modes, respectively, n_4 and n_5 represent the two bending modes, and n_6 is the out-of-plane bending quantum number. These quantum numbers can be straightforwardly mapped onto the normal mode quantum numbers v$_1$, v$_2$, v$_3$, v$_4$, v$_5$, and v$_6$ conventionally used in most spectroscopic studies. In the normal mode notation, the H_2CO vibrational states are labelled as $\mathrm{v}_1\nu_1 + \mathrm{v}_2\nu_2 + \mathrm{v}_3\nu_3 + \mathrm{v}_4\nu_4 + \mathrm{v}_5\nu_5 + \mathrm{v}_6\nu_6$. The normal modes are defined as follows. A_1 symmetry: ν_1 is the symmetric C–H stretching mode (E_{ν_1} = 2782.46 cm^{-1}), ν_2 is the C–O stretching mode (E_{ν_2} = 1746.01 cm^{-1}), ν_3 is the symmetric O–C–H bending mode (E_{ν_3} = 1500.18 cm^{-1}); B_1 symmetry: ν_4 is the out-of-plane bending mode associated with the coordinate τ (E_{ν_4} = 1167.26 cm^{-1}); B_2 symmetry: ν_5 is the asymmetric C–H stretching C–H mode (E_{ν_5} = 2843.30 cm^{-1}), and ν_6 is the asymmetric bending O–C–H mode (E_{ν_6} = 1249.09 cm^{-1}). The values given above in parentheses are the experimental fundamental term values

TABLE VII. Residuals (Obs.−Calc.; in cm^{-1}) for pure rotational term values with $J \leq 5$, computed with TROVE from the *ab initio* AVQZ (A) and refined H_2CO-2011 (R) PESs. The corresponding rms errors are 0.094 cm^{-1} and 0.004 cm^{-1}, respectively. The "observed" ground state energy levels are from Ref. 30 obtained there using the spectroscopic parameters from Ref. 51.

J	K_a	K_b	τ	Γ	Obs.	Calc.(A)	Obs.–Calc.(A)	Calc.(R)	Obs.–Calc.(R)
0	0	0	0	A_1	0.0000	0.0000	0.0000	0.0000	0.0000
1	0	1	1	A_2	2.4296	2.4182	0.0114	2.4291	0.0005
1	1	1	0	B_1	10.5390	10.5316	0.0074	10.5396	−0.0006
1	1	0	1	B_2	10.7001	10.6916	0.0085	10.7009	−0.0008
2	0	2	0	A_1	7.2864	7.2523	0.0341	7.2848	0.0016
2	2	2	0	A_1	40.0428	40.0219	0.0209	40.0454	−0.0026
2	2	1	1	A_2	40.0404	40.0195	0.0209	40.0430	−0.0026
2	1	2	0	B_1	15.7202	15.6878	0.0324	15.7202	0.0000
2	1	2	1	B_2	15.2369	15.2078	0.0291	15.2361	0.0008
3	2	3	0	A_1	47.3278	47.2730	0.0548	47.3289	−0.0011
3	0	3	1	A_2	14.5655	14.4975	0.0680	14.5623	0.0032
3	2	1	1	A_2	47.3397	47.2847	0.0550	47.3408	−0.0011
3	1	3	0	B_1	22.2822	22.2206	0.0616	22.2794	0.0028
3	3	3	0	B_1	88.2382	88.2004	0.0378	88.2434	−0.0052
3	1	2	1	B_2	23.2487	23.1805	0.0682	23.2474	0.0013
3	3	0	1	B_2	88.2382	88.2005	0.0377	88.2434	−0.0052
4	0	4	0	A_1	24.2597	24.1465	0.1132	24.2542	0.0055
4	2	4	0	A_1	57.0780	56.9773	0.1007	57.0771	0.0009
4	4	4	0	A_1	155.1694	155.1105	0.0589	155.1752	−0.0058
4	2	3	1	A_2	57.0425	56.9422	0.1003	57.0414	0.0011
4	4	1	1	A_2	155.1694	155.1105	0.0589	155.1752	−0.0058
4	1	4	0	B_1	33.2835	33.1678	0.1157	33.2807	0.0028
4	3	4	0	B_1	97.9578	97.8745	0.0833	97.9608	−0.0030
4	1	4	1	B_2	31.6729	31.5682	0.1047	31.6674	0.0055
4	3	2	1	B_2	97.9577	97.8743	0.0834	97.9606	−0.0029
5	2	5	0	A_1	69.1825	69.0254	0.1571	69.1787	0.0038
5	4	5	0	A_1	167.3247	167.1988	0.1259	167.3177	0.0070
5	0	5	1	A_2	36.3592	36.1899	0.1693	36.3510	0.0082
5	2	3	1	A_2	69.2653	69.1071	0.1582	69.2618	0.0035
5	4	1	1	A_2	167.3247	167.1988	0.1259	167.3177	0.0070
5	1	5	0	B_1	43.4067	43.2480	0.1587	43.3978	0.0089
5	3	5	0	B_1	110.1086	109.9683	0.1403	110.1088	−0.0002
5	5	5	0	B_1	240.7771	240.6934	0.0837	240.7792	−0.0021
5	1	4	1	B_2	45.8219	45.6468	0.1751	45.8171	0.0048
5	3	2	1	B_2	110.1104	109.9689	0.1415	110.1095	0.0010
5	5	0	1	B_2	240.7771	240.6934	0.0837	240.7792	−0.0021

from Refs. 31 and 35. The quantum numbers v_1, v_2, v_3, v_4, v_5, and v_6 count the excitations of the corresponding modes.

IV. THE REFINED POTENTIAL ENERGY SURFACE

We have extended the program TROVE to allow for the direct fitting of the potential energy surface to experimental ro-vibrational term values. Details of the procedure are given in Ref. 9. The basic idea is to describe the refinement in terms of a correction ΔV to the initial *ab initio* PES V. That is, the refined PES V' can be written as $V' = V + \Delta V$, and now the eigenfunctions of the initial Hamiltonian H are used as basis functions for the diagonalization of the extended Hamiltonian $H' = H + \Delta V$. In this basis set, the only off-diagonal Hamiltonian term is ΔV, which we expand in analogy to Eq. (1), that is, by the expansion of the form already used for V. The corresponding expansion coefficients Δf_{ijklmn} are obtained by the least-squares fitting starting from $\Delta V = 0$.

In the PES fittings, we use as input data "experimental" energies derived from the corresponding experimental transition wavenumbers or frequencies. In order to determine from experimental wavenumber data, for example, the upper state energy of an absorption transition for inclusion in our PES-fitting input data set, we must know the assignment of the transition and the energy of the lower state. The accuracy of the determined upper state energy will reflect both the accuracy of the experimental wavenumber and that of the lower state energy. Correct assignments of the experimentally observed transitions are required in order that we can identify the upper and lower state energies involved in a given observed transition and correlate each experimentally derived energy with a calculated energy. In the present work on H_2CO, it was straightforward to correlate the theoretically calculated and the experimentally derived energies because, as mentioned

TABLE VIII. Number N of experimentally determined energy levels of H_2CO employed presently.[a] Some energies were not included in the input data set in order to speed up the fitting procedure.

J	N	rms (cm^{-1})	References	Comment
0	18	0.073	29, 30, and 32	
1	45	0.018	29, 30, and 32	
2	75	0.017	29, 30, and 32	
3	94	0.024	29, 30, and 32	Not used in fittings
4	118	0.040	29, 30, and 32	Not used in fittings
5	142	0.055	29, 30, and 32	A_1, B_2 not used in fittings
Total	492	0.040		Excluding band centers from Refs. 24, 31, 33, and 34
0	107	1.653	24, 31, 33, and 34	Below 7500 cm^{-1}

[a] For each set of energy levels we give the angular momentum quantum number J, the rms error attained in the fitting of the H_2CO-2011 PES (see below), and the references to the experimental data.

above, using the initial *ab initio* PES AVQZ we obtained theoretical energies in a very good agreement with the experimentally derived ones. That is, the pattern of the ro-vibrational energies obtained in the initial theoretical calculation could immediately be identified with the pattern of experimentally derived energies. All we had to do was to verify that each ro-vibrational level was assigned experimentally as belonging to a state with values of the good quantum numbers J and Γ (where Γ is the ro-vibrational symmetry in the MS group) that match the values for the correlating theoretically calculated level.

We include in the input dataset for the PES fitting all experimentally known term values of H_2CO with $J \leq 5$. Table VIII gives various statistical information about the selected input data. We outline briefly the sources of these data. The current (2008) version of the HITRAN database contains experimentally derived energies for H_2CO in three regions: the pure rotational term values, the term values of the ν_2 state around 1740 cm^{-1}, and the term values for the states ν_1, $\nu_2+\nu_4$, $2\nu_3$, $\nu_2+\nu_6$, $\nu_3+\nu_6$, $\nu_3+\nu_4$, ν_5, and $2\nu_6$ between 2600 cm^{-1} and 3000 cm^{-1}. It is known that the H_2CO data in HITRAN are far from being complete and so we decided not to use HITRAN data as input for our PES fitting. Instead, we have explored other, more up-to-date sources of the experimental information. Recently, Tchana *et al.*[30] reported an experimental line list for the ν_2, ν_3, ν_4, and ν_6 transitions of formaldehyde. Perrin *et al.*[29] published a very accurate synthetic line list covering the band systems (ν_2, ν_3, ν_4, ν_6) and (ν_1, $\nu_2+\nu_3$, $\nu_2+\nu_4$, $\nu_2+\nu_6$, $2\nu_3$, $\nu_3+\nu_4$, $\nu_3+\nu_6$, $2\nu_4$, $\nu_4+\nu_6$, ν_5, $2\nu_6$) in the 5.7 μm and 3.6 μm regions, respectively. Perez *et al.*[32] measured a set of hot transitions belonging to the bands $\nu_4-\nu_4$, $\nu_1+\nu_4-\nu_4$, and $\nu_4+\nu_5-\nu_4$. These transitions involve states not present in the line compilations of Tchana *et al.*[30] and Perrin *et al.*[29] For our input dataset, we selected 492 energy levels with $J \leq 5$ from Refs. 29, 30, and 32. In the fitting, we assigned weights of $w_i = 100.0$ to the purely rotational energy levels and $w_i = 1.0$ to levels in excited vibrational states. We chose higher weights for the rotational energies in order to ensure an accurate determination of the equilibrium structure, since accurate structural parameter values are important for the reliable prediction of the ro-vibrational term values at high J values.

Energies of vibrationally excited states are important for the determination of the PES since increasing vibrational excitation causes increasing vibrational amplitudes. Consequently, when the input data set for the fitting involves highly excited vibrational states, the high-energy part of the PES is sampled by the corresponding data. For this reason, we included in the input data set the vibrational band centers of H_2CO from the dispersed fluorescence study by Bouwens *et al.*[24] in spite of their relatively low accuracy (standard deviation of 1.7 cm^{-1}). We selected the term values below 7500 cm^{-1} and weighted them by 0.1. Some of the 3.5 μm-region band centers of Ref. 24 corresponding to the states (ν_1, $\nu_2+\nu_3$, $\nu_2+\nu_4$, $\nu_2+\nu_6$, $2\nu_3$, $\nu_3+\nu_4$, $\nu_3+\nu_6$, $2\nu_4$, $\nu_4+\nu_6$, ν_5, and $2\nu_6$) were recently re-determined at a higher accuracy by Perrin *et al.*[31] Similar improvements were made by Flaud *et al.*[33] for the ($\nu_1+\nu_2$, $\nu_1+\nu_6$, $3\nu_2$, $\nu_2+\nu_5$, $2\nu_2+\nu_6$, $\nu_2+\nu_4+\nu_6$, $\nu_3+\nu_5$, and $2\nu_3+\nu_6$) states in the 1.9–2.56 μm region. In addition, the $2\nu_5$ band was reinvestigated by Saha *et al.*[34] These recent band center values[31,33,34] were used in place of the corresponding $J = 0$ energies from Ref. 24.

In total, our input data set comprised 599 energies. For the actual refinement, we used only 319 energies with $J = 0, 1, 2$ (all symmetries) and $J = 5$ (A_2 and B_1 symmetry) in order to speed up the fitting procedure. The comparison of the theoretical and experimental energies with ensuing statistical analysis was carried out for all 599 experimental energies.

In the refinement, we constrain the fitted PES to follow roughly the shape of the initial AVQZ PES of H_2CO. This is achieved by simultaneously fitting the f_{ijklmn} parameters to the *ab initio* points V_i and to the experimental energy levels.[50] The simultaneous fitting has a dual purpose: first, it ensures that the PES retain a physically acceptable shape and second, it allows all potential parameters to be varied irrespective of the amount of the experimental data available for particular vibrational excitations.[50] The refined parameter values characterizing the new "spectroscopic" PES of H_2CO (which we refer to as H_2CO-2011) are given in the supplementary material to the present paper,[43] together with a Fortran 90 routine that generates values of the potential energy function. It should be noted that we do not vary the structural parameters a_i^{ref} in our fitting procedure. Instead, the equilibrium geometry is adjusted by varying the linear expansion constants f_{10000}, f_{01000} ($= f_{00100}$), and f_{00100} ($= f_{00010}$), which are zero in the case of the *ab initio* PES. The PES refinement thus results in a new semi-empirical equilibrium structure with $r^{\mathrm{e}}_{\mathrm{CO}} = 1.20367$ Å, $r^{\mathrm{e}}_{\mathrm{CH}} = 1.10290$ Å, and $\theta^{\mathrm{e}} = 121.781°$. These values are very similar to the *ab initio* AVQZ equilibrium parameters (see Table I).

Comparing the *ab initio* and the refined values of the potential parameters, there are rather small deviations for the quadratic diagonal terms (less than 2% in the case of f_{20000}, f_{02000}, and f_{00200}, and 9% in the case of f_{00002}), while some of the other (especially higher-order) parameters show larger percentage deviations. It is, however, more relevant to compare the *ab initio* and the refined PES directly. The rms

TABLE IX. Residuals (Obs.−Calc.; in cm^{-1}) for selected $J = 2$ ($\Gamma = A_1, A_2$) and $J = 4$ (A_1) energy levels of H_2CO, computed with TROVE from the refined H_2CO-2011 PES. See the supplementary material for a complete list (Ref. 43). The "observed" energy levels are from Refs. 29, 30, and 32.

J	Γ	K	State	Obs.	Calc.	Obs.–Calc.	J	Γ	K	State	Obs.	Calc.	Obs.–Calc.
2	A_1	0	Ground state	7.286	7.285	0.002	4	A_1	0	Ground state	24.260	24.254	0.005
2	A_1	2	Ground state	40.043	40.045	− 0.003	4	A_1	2	Ground state	57.078	57.077	0.001
2	A_1	1	ν_4	1181.584	1181.612	− 0.028	4	A_1	4	Ground state	155.169	155.175	− 0.006
2	A_1	1	ν_6	1265.614	1265.594	0.020	4	A_1	1	ν_4	1198.999	1199.010	− 0.012
2	A_1	0	ν_3	1507.483	1507.508	− 0.025	4	A_1	3	ν_4	1254.369	1254.290	0.079
2	A_1	2	ν_3	1540.469	1540.475	− 0.006	4	A_1	1	ν_6	1282.007	1281.991	0.016
2	A_1	0	ν_2	1753.247	1753.250	− 0.003	4	A_1	3	ν_6	1357.492	1357.496	− 0.004
2	A_1	2	ν_2	1786.013	1786.033	− 0.019	4	A_1	0	ν_3	1524.504	1524.557	− 0.054
2	A_1	0	$\nu_3 + \nu_6$	2501.618	2501.608	0.010	4	A_1	2	ν_3	1557.564	1557.603	− 0.038
2	A_1	1	$\nu_3 + \nu_4$	2680.851	2680.853	− 0.002	4	A_1	4	ν_3	1656.329	1656.303	0.026
2	A_1	1	$2\nu_3$	2736.240	2736.234	0.006	4	A_1	0	ν_2	1770.105	1770.078	0.027
2	A_1	0	ν_1	2789.742	2789.747	− 0.006	4	A_1	2	ν_2	1802.935	1802.921	0.013
2	A_1	2	ν_1	2821.865	2821.861	0.004	4	A_1	4	ν_2	1901.055	1901.085	− 0.030
2	A_1	1	ν_5	2858.367	2858.359	0.008	4	A_1	1	$\nu_3 + \nu_4$	2698.307	2698.323	− 0.017
2	A_1	1	$\nu_2 + \nu_4$	2920.755	2920.749	0.006	4	A_1	3	$\nu_3 + \nu_4$	2751.225	2751.272	− 0.047
2	A_1	0	$\nu_3 + \nu_6$	3006.318	3006.303	0.016	4	A_1	1	$2\nu_3$	2752.706	2752.720	− 0.014
2	A_1	1	$\nu_2 + \nu_6$	3016.219	3016.227	− 0.008	4	A_1	0	ν_1	2806.711	2806.717	− 0.006
2	A_1	2	$\nu_3 + \nu_6$	3039.511	3039.492	0.019	4	A_1	3	$2\nu_3$	2830.592	2830.562	0.030
2	A_1	1	$\nu_1 + \nu_4$	3955.706	3955.712	− 0.007	4	A_1	2	ν_1	2838.930	2838.957	− 0.027
2	A_1	2	$\nu_4 + \nu_5$	4030.369	4030.410	− 0.041	4	A_1	1	ν_5	2874.756	2874.731	0.025
2	A_2	2	Ground state	40.040	40.043	− 0.003	4	A_1	4	ν_1	2935.100	2935.056	0.044
2	A_2	1	ν_4	1181.160	1181.190	− 0.030	4	A_1	1	$\nu_2 + \nu_4$	2938.072	2938.003	0.068
2	A_2	1	ν_6	1266.111	1266.093	0.019	4	A_1	3	ν_5	2939.626	2939.687	− 0.061
2	A_2	2	ν_3	1540.466	1540.472	− 0.007	4	A_1	3	$\nu_2 + \nu_4$	2996.977	2996.972	0.005
2	A_2	2	ν_2	1786.012	1786.030	− 0.019	4	A_1	0	$\nu_3 + \nu_6$	3023.382	3023.431	− 0.048
2	A_2	1	$\nu_3 + \nu_4$	2680.424	2680.423	0.001	4	A_1	1	$\nu_2 + \nu_6$	3032.507	3032.496	0.011
2	A_2	1	$2\nu_3$	2736.757	2736.764	− 0.007	4	A_1	2	$\nu_3 + \nu_6$	3056.667	3056.721	− 0.053
2	A_2	2	ν_1	2821.867	2821.858	0.009	4	A_1	3	$\nu_2 + \nu_6$	3106.050	3106.043	0.008
2	A_2	1	ν_5	2858.856	2858.847	0.009	4	A_1	4	$\nu_3 + \nu_6$	3156.042	3156.063	− 0.021
2	A_2	1	$\nu_2 + \nu_4$	2920.322	2920.327	− 0.005	4	A_1	1	$\nu_1 + \nu_4$	3973.122	3973.134	− 0.012
2	A_2	1	$\nu_2 + \nu_6$	3016.724	3016.721	0.003	4	A_1	2	$\nu_4 + \nu_5$	4047.248	4047.252	− 0.003
2	A_2	2	$\nu_3 + \nu_6$	3039.511	3039.489	0.022							
2	A_2	1	$\nu_1 + \nu_4$	3955.272	3955.275	− 0.003							
2	A_2	0	$\nu_4 + \nu_5$	4003.754	4003.765	− 0.011							
2	A_2	2	$\nu_4 + \nu_5$	4030.371	4030.413	− 0.042							

deviations between the corresponding individual energies at the grid points are found to increase with increasing energy (relative to the equilibrium energy): For *ab initio* points with energies below 10 000 cm^{-1}, 20 000 cm^{-1}, and 30 000 cm^{-1}, the rms deviations are 120 cm^{-1}, 160 cm^{-1}, and 210 cm^{-1}, respectively.

V. RESULTS AND CONCLUSIONS

The TROVE-calculated vibrational term values obtained with the H_2CO-2011 PES are included in Tables III–VI (relative to the calculated zero point energy of 5774.05 cm^{-1}) and compared with the corresponding experimental data and the *ab initio* AQVZ values from this work. Tables IX–XI give the residuals (Obs.−Calc.) for selected states; a complete list is given in the supplementary material.[43] Graphical representations of the agreement between the theoretical and experimental energies are shown in Figs. 2 and 3, where the residuals are displayed for all $J = 0, 1, 2, 3, 4, 5$ term values that have experimental counterparts, including those not considered in the fitting. The total rms error for all energy levels except the $J = 0$ set from Bouwens *et al.*[24] is 0.040 cm^{-1} (for further details see Table VIII). The largest deviation of 0.3 cm^{-1} (see Fig. 2) is found for the $\nu_4 + \nu_6$ band center ($J = 0$). We sus-

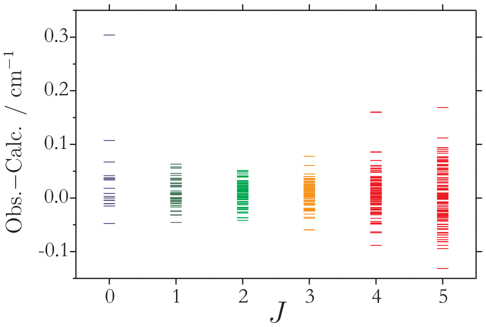

FIG. 2. Residuals (Obs.−Calc.) for the $J \geq 0$ term values of H_2CO, obtained with TROVE and the refined PES H_2CO–2011 (see text). The residuals associated with the vibrational band centers from Refs. 24, 31, 33, and 34 are excluded.

TABLE X. Residuals (Obs.−Calc.; in cm^{-1}) for selected $J = 5$ energy levels of H_2CO, computed with TROVE from the refined H_2CO-2011 PES. See the supplementary material for a complete list (Ref. 43). The "observed" energy levels are from Refs. 29, 30, and 32.

J	Γ	K	State	Obs.	Calc.	Obs.–Calc.	J	Γ	K	State	Obs.	Calc.	Obs.–Calc.
5	A_1	2	Ground state	69.182	69.179	0.004	5	B_1	1	Ground state	43.407	43.398	0.009
5	A_1	4	Ground state	167.325	167.318	0.007	5	B_1	3	Ground state	110.109	110.109	0.000
5	A_1	1	ν_4	1209.313	1209.325	−0.012	5	B_1	5	Ground state	240.777	240.779	−0.002
5	A_1	3	ν_4	1266.466	1266.379	0.087	5	B_1	2	ν_4	1231.188	1231.157	0.032
5	A_1	1	ν_6	1296.198	1296.190	0.007	5	B_1	0	ν_6	1285.408	1285.392	0.015
5	A_1	3	ν_6	1369.614	1369.620	−0.007	5	B_1	4	ν_4	1316.675	1316.516	0.158
5	A_1	5	ν_6	1514.745	1514.723	0.022	5	B_1	2	ν_6	1323.189	1323.264	−0.075
5	A_1	2	ν_3	1569.702	1569.760	−0.058	5	B_1	4	ν_6	1433.619	1433.621	−0.002
5	A_1	4	ν_3	1668.521	1668.517	0.004	5	B_1	1	ν_3	1543.659	1543.700	−0.042
5	A_1	2	ν_2	1814.957	1814.922	0.035	5	B_1	3	ν_3	1610.920	1610.954	−0.034
5	A_1	4	ν_2	1913.119	1913.125	−0.006	5	B_1	5	ν_3	1742.477	1742.420	0.058
5	A_1	1	$\nu_3 + \nu_4$	2708.628	2708.642	−0.015	5	B_1	1	ν_2	1789.164	1789.137	0.027
5	A_1	3	$\nu_3 + \nu_4$	2763.354	2763.413	−0.059	5	B_1	3	ν_2	1855.896	1855.879	0.017
5	A_1	1	$2\nu_3$	2767.034	2767.125	−0.091	5	B_1	5	ν_2	1986.603	1986.634	−0.031
5	A_1	3	$2\nu_3$	2842.751	2842.720	0.031	5	B_1	2	$\nu_3 + \nu_4$	2729.309	2729.351	−0.042
5	A_1	2	ν_1	2851.050	2851.099	−0.049	5	B_1	0	$2\nu_3$	2755.631	2755.695	−0.064
5	A_1	5	$\nu_3 + \nu_4$	2877.620	2877.678	−0.058	5	B_1	5	$\nu_3 + \nu_6$	2791.651	2791.631	0.020
5	A_1	1	ν_5	2888.900	2888.856	0.044	5	B_1	2	$2\nu_3$	2795.228	2795.261	−0.033
5	A_1	4	ν_1	2947.231	2947.178	0.053	5	B_1	4	$\nu_3 + \nu_4$	2812.663	2812.730	−0.068
5	A_1	1	$\nu_2 + \nu_4$	2948.280	2948.219	0.061	5	B_1	1	ν_1	2825.676	2825.668	0.008
5	A_1	3	ν_5	2951.745	2951.792	−0.047	5	B_1	0	ν_5	2879.596	2879.543	0.053
5	A_1	5	$2\nu_3$	2989.064	2989.131	−0.067	5	B_1	3	ν_1	2891.108	2891.052	0.056
5	A_1	3	$\nu_2 + \nu_4$	3009.004	3008.964	0.040	5	B_1	4	$2\nu_3$	2907.673	2907.733	−0.060
5	A_1	1	$\nu_2 + \nu_6$	3046.646	3046.577	0.068	5	B_1	2	ν_5	2911.800	2911.796	0.004
5	A_1	2	$\nu_3 + \nu_6$	3068.840	3068.937	−0.097	5	B_1	2	$\nu_2 + \nu_4$	2971.601	2971.530	0.070
5	A_1	5	ν_5	3079.477	3079.581	−0.104	5	B_1	4	ν_5	3007.671	3007.762	−0.091
5	A_1	3	$\nu_2 + \nu_6$	3118.100	3118.071	0.029	5	B_1	5	ν_1	3019.289	3019.216	0.073
5	A_1	5	$\nu_2 + \nu_4$	3130.633	3130.731	−0.098	5	B_1	0	$\nu_2 + \nu_6$	3036.146	3036.091	0.055
5	A_1	4	$\nu_3 + \nu_6$	3168.285	3168.354	−0.069	5	B_1	1	$\nu_3 + \nu_6$	3042.557	3042.608	−0.050
5	A_1	5	$\nu_2 + \nu_6$	3260.950	3260.922	0.028	5	B_1	4	$\nu_2 + \nu_4$	3061.890	3061.903	−0.013
5	A_1	0	$\nu_4 + \nu_5$	4032.623	4032.585	0.038	5	B_1	2	$\nu_2 + \nu_6$	3072.862	3072.821	0.040
5	A_1	3	$\nu_1 + \nu_4$	4038.166	4038.128	0.038	5	B_1	3	$\nu_3 + \nu_6$	3110.325	3110.412	−0.087
5	A_1	2	$\nu_4 + \nu_5$	4059.382	4059.365	0.017	5	B_1	4	$\nu_2 + \nu_6$	3180.935	3180.912	0.023

pect the corresponding "experimental" value from Ref. 31 to be an outlier since all other experimental ro-vibrational term values from this band[29] are reproduced to better than 0.05 cm^{-1}. The band centers from Bouwens *et al.*[24] (below 7500 cm^{-1}) are reproduced with an rms error of 1.65 cm^{-1}, close to the quoted accuracy of the experimental data (see above). In order to estimate how our new refined PES performs in extrapolations to higher J values, we have generated the ro-vibrational energies for $J = 6$. Comparison with the available experimental term values[29,30,32] yields a rms error of 0.08 cm^{-1} for 167 $J = 6$ ro-vibrational term values, all below 4100 cm^{-1}. This indicates that the refined PES remains reasonable for moderate extrapolations to somewhat higher J values. Calculations for much higher J values quickly become more demanding and will require larger basis sets than used presently.

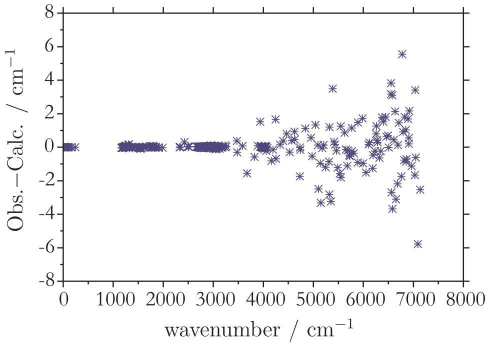

FIG. 3. Residuals (Obs.−Calc.) for the $J = 0$ term values of H_2CO, obtained with TROVE and the refined PES H_2CO-2011 (see text).

It should also be noted at this point that the variational TROVE calculations employed in the PES fitting of the present work are not fully converged because of the basis set truncation at $P_{\max} = 14$ and the internal use of Taylor-type expansions of the Hamiltonian operator truncated after the 8th-order terms (see Sec. III). Therefore, our refined PES H_2CO-2011 is "effective" in the sense that the stated accuracy of 0.04 cm^{-1} can only be guaranteed when the H_2CO-2011 PES is used in conjunction with the same calculation setup as described in Sec. III.

We have generated a "spectroscopic" PES of H_2CO which reproduces the available experimental ro-vibrational energies of this molecule with an unprecedented accuracy. We

TABLE XI. Residuals (Obs.−Calc.; in cm^{-1}) for selected $J = 5$ energy levels of H_2CO, computed with TROVE from the refined H_2CO-2011 PES. See the supplementary material for a complete list (Ref. 43). The "observed" energy levels are from Refs. 29, 30, and 32.

J	Γ	K	State	Obs.	Calc.	Obs.–Calc.	J	Γ	K	State	Obs.	Calc.	Obs.–Calc.
5	A_2	0	g.s.	36.359	36.351	0.008	5	B_1	5	$\nu_3+\nu_6$	3242.685	3242.728	−0.043
5	A_2	2	g.s.	69.265	69.262	0.004	5	B_1	2	$\nu_4+\nu_5$	4004.845	4004.887	−0.042
5	A_2	4	g.s.	167.325	167.318	0.007	5	B_1	1	$\nu_1+\nu_4$	4040.305	4040.262	0.042
5	A_2	1	ν_4	1211.431	1211.432	0.000	5	B_2	1	g.s.	45.822	45.817	0.005
5	A_2	3	ν_4	1266.466	1266.380	0.087	5	B_2	3	g.s.	110.110	110.109	0.001
5	A_2	1	ν_6	1293.712	1293.699	0.013	5	B_2	5	g.s.	240.777	240.779	−0.002
5	A_2	3	ν_6	1369.614	1369.620	−0.006	5	B_2	0	ν_4	1203.449	1203.469	−0.020
5	A_2	5	ν_6	1514.745	1514.723	0.022	5	B_2	2	ν_4	1231.267	1231.236	0.032
5	A_2	0	ν_3	1536.634	1536.707	−0.073	5	B_2	4	ν_4	1316.675	1316.516	0.158
5	A_2	2	ν_3	1569.797	1569.860	−0.063	5	B_2	2	ν_6	1323.189	1323.188	0.000
5	A_2	4	ν_3	1668.521	1668.517	0.004	5	B_2	4	ν_6	1433.619	1433.621	−0.002
5	A_2	0	ν_2	1782.122	1782.074	0.048	5	B_2	1	ν_3	1546.255	1546.358	−0.103
5	A_2	2	ν_2	1815.041	1815.003	0.038	5	B_2	3	ν_3	1610.920	1610.955	−0.035
5	A_2	4	ν_2	1913.119	1913.125	−0.006	5	B_2	5	ν_3	1742.477	1742.420	0.057
5	A_2	1	$\nu_3+\nu_4$	2710.766	2710.794	−0.028	5	B_2	1	ν_2	1791.598	1791.532	0.066
5	A_2	3	$\nu_3+\nu_4$	2763.301	2763.352	−0.052	5	B_2	3	ν_2	1855.896	1855.879	0.016
5	A_2	1	$2\nu_3$	2764.503	2764.536	−0.033	5	B_2	5	ν_2	1986.603	1986.634	−0.031
5	A_2	0	ν_5	2818.805	2818.811	−0.006	5	B_2	0	$\nu_3+\nu_4$	2703.300	2703.314	−0.013
5	A_2	3	$2\nu_3$	2842.751	2842.721	0.030	5	B_2	2	$\nu_3+\nu_4$	2729.408	2729.452	−0.044
5	A_2	2	ν_5	2851.138	2851.189	−0.051	5	B_2	5	$\nu_3+\nu_6$	2791.651	2791.631	0.020
5	A_2	5	$\nu_3+\nu_4$	2877.620	2877.678	−0.058	5	B_2	2	$2\nu_3$	2795.151	2795.181	−0.030
5	A_2	1	ν_1	2886.456	2886.419	0.037	5	B_2	4	$\nu_3+\nu_4$	2812.662	2812.730	−0.068
5	A_2	4	ν_5	2947.231	2947.178	0.053	5	B_2	1	ν_5	2828.148	2828.175	−0.027
5	A_2	1	$\nu_2+\nu_4$	2950.430	2950.319	0.111	5	B_2	3	ν_5	2891.108	2891.052	0.055
5	A_2	3	ν_1	2951.745	2951.797	−0.051	5	B_2	4	$2\nu_3$	2907.672	2907.733	−0.062
5	A_2	5	$2\nu_3$	2989.064	2989.131	−0.067	5	B_2	2	ν_1	2911.713	2911.709	0.003
5	A_2	3	$\nu_2+\nu_4$	3009.004	3008.964	0.040	5	B_2	0	$\nu_2+\nu_4$	2941.927	2941.842	0.085
5	A_2	0	$\nu_3+\nu_6$	3035.539	3035.630	−0.091	5	B_2	2	$\nu_2+\nu_4$	2971.676	2971.602	0.074
5	A_2	1	$\nu_2+\nu_6$	3044.133	3044.113	0.020	5	B_2	4	ν_1	3007.671	3007.762	−0.091
5	A_2	2	$\nu_3+\nu_6$	3068.947	3069.053	−0.106	5	B_2	5	ν_5	3019.289	3019.216	0.073
5	A_2	5	ν_1	3079.477	3079.581	−0.104	5	B_2	1	$\nu_3+\nu_6$	3045.316	3045.475	−0.159
5	A_2	3	$\nu_2+\nu_6$	3118.100	3118.071	0.030	5	B_2	4	$\nu_2+\nu_4$	3061.890	3061.903	−0.013
5	A_2	5	$\nu_2+\nu_4$	3130.633	3130.731	−0.098	5	B_2	2	$\nu_2+\nu_6$	3072.782	3072.744	0.038
5	A_2	4	$\nu_3+\nu_6$	3168.285	3168.354	−0.069	5	B_2	3	$\nu_3+\nu_6$	3110.325	3110.413	−0.088
5	A_2	5	$\nu_2+\nu_6$	3260.950	3260.922	0.028	5	B_2	4	$\nu_2+\nu_6$	3180.935	3180.912	0.023
5	A_2	1	$\nu_4+\nu_5$	3985.538	3985.569	−0.031	5	B_2	5	$\nu_3+\nu_6$	3242.685	3242.728	−0.043
5	A_2	3	$\nu_4+\nu_5$	4038.166	4038.128	0.038	5	B_2	0	$\nu_4+\nu_5$	3977.681	3977.653	0.028
5	A_2	2	$\nu_1+\nu_4$	4059.300	4059.274	0.026	5	B_2	2	$\nu_4+\nu_5$	4004.929	4004.973	−0.045

are planning to use this PES in comprehensive line list calculations. Another future application is the detailed assignment of the experimental transitions in the 1.5 μm region, which have been extensively investigated by high-resolution spectroscopy owing to the development of monochromatic diode lasers operating near this wavelength (see, for example, Refs. 52 and 53).

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