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The Electronic Spectrum of H_2COH Revisited

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The electronic spectrum of the H_2COH radical has been reinvestigated using the MRDCI method, an AO basis set containing two sets of s and p Rydberg functions, and diagonalized CI spaces on the order of 2.5×10^5. A detailed analysis of the calculations reveals that excitation energies obtained with truncated CI spaces overestimate the corresponding extrapolated and estimated full CI energies. The new results confirm the assignment made earlier by us on the basis of less extensive calculations: experimental T_0 values of 4.34 and 5.09 eV correspond to the excitations $\pi^* \rightarrow 3p_x$ and $\pi^* \rightarrow 3p_z$, respectively. As previously predicted, the $\pi^* \rightarrow 3p_z$ system has been shown experimentally to be polarized along the CO bond.

Introduction

In a recent ab initio multireference configuration interaction (MRDCI) study carried out by us—and published in this journal (hereafter, Paper I)[1]—several properties of the hydroxymethyl radical (H_2COH) were reported, including equilibrium geometries, vibrational frequencies, ionization potentials (IP), electronic transition energies (ΔE), dipole moments, spin densities, Fermi contact terms, and electron-spin *g*-factors.

In that study, four conformations were considered: (1) H_2COH(eq), corresponding to the totally nonsymmetrical (C_1) equilibrium geometry; (2) H_2COH(i), the planar inversion conformation of $C_s(xy)$ symmetry, which lies ~0.03 eV above equilibrium; (3) H_2COH(r), the rotation isomer with $C_s(xz)$ symmetry placed at about 0.20 eV; and (4) H_2COH(ion), located at 0.45 eV. This corresponds to the equilibrium geometry of H_2COH^+ in its X^1A' ground state (GS), which is structurally similar to that of planar H_2COH(i) but with different bond distances and angles (particularly, a shorter R(CO)). The equilibrium geometries of the Rydberg states were assumed to be fairly well described by the H_2COH(ion) geometry.

In the system of coordinates used in this work, taking planar H_2COH(i) as an example, x and y lie in the symmetry plane, and x is collinear to the CO bond. Earlier, we considered a different axis orientation, with the roles of x and z exchanged relative to the convention adopted here, cf Figure 1 in Paper I. Literature results, if necessary, will be adapted to the present nomenclature.

Before our study appeared, only one theoretical work on the electronic spectrum of H_2COH was available, namely, that carried out by Rettrup et al.,[2] who calculated vertical ΔE's for the 3s,3p states of H_2COH(eq). Their assignment of two experimental T_0 values, however, was faulty because of the large difference between vertical and adiabatic ΔE's (see below).

In Paper I, the first excited state, which corresponds to $1^2A'(\pi^* \rightarrow 3s)$ at the H_2COH(ion) geometry, was found to lie adiabatically at $T_e = 3.23$ eV. This is about 1 eV smaller than the lowest ΔE experimentally recorded so far ($T_0 = 4.34$ eV),[3] which was previously assumed to be the $\pi^* \rightarrow 3s$ transition. We reassigned the observed band to the next excited state, $2^2A'(\pi^* \rightarrow 3p_x)$, for which $T_e = 4.09$ eV was calculated ($T_0 = 4.23$ eV after zero-point energy (ZPE) corrections).

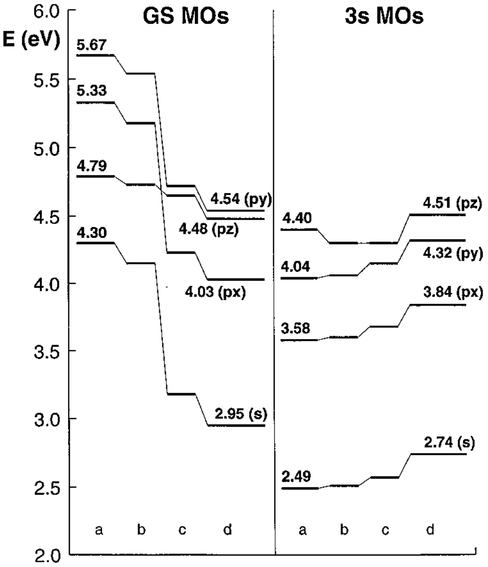

Figure 1. Relative energies for the 3s,3p Rydberg states of H_2COH at the H_2COH(ion) geometry, using $X^2A''(\pi^*)$ GS and $1^2A'(\pi^* \rightarrow 3s)$ MOs. The values shown are: $a = \Delta E(T_1)$, $b = \Delta E(T_2)$, $c = \Delta E_{\text{extrap}}$, and $d = \Delta E_{\text{FCI}}$. Each ΔE is relative to the energy of the GS obtained under the same conditions as those for the excited states, including geometry.

Similarly, a T_0(expt.) of 5.09 eV[3−5] was reassigned to $\pi^* \rightarrow 3p_z$, or $2^2A'' \leftarrow X^2A''$, on the basis of a calculated $T_e = 5.06$ eV ($T_0 = 5.20$ eV). Previously, it was assumed that this band is due to $\pi^* \rightarrow 3p_x$, but, as said above, such excitation gives rise to the lower absorption at 4.34 eV.

The old assignment[3] was based on calculated vertical ΔE's,[2] which were erroneusly compared with experimental adiabatic values. From the photoionization spectrum of H_2COH, it is known that the difference between the vertical and adiabatic IP's is about 0.60 eV.[6] A similar energy difference should apply to Rydberg states, as was confirmed in our previous investigation. Summing up, we classified the two experimental bands as $\pi^* \rightarrow 3p$, the energetically lowest being $3p_x(1^2A')$ and the higher one being $3p_z(2^2A'')$. Relative to the CO bond, they constitute perpendicular- and parallel-polarized bands, respectively. According to the old assignment, both $3s(1^2A')$ and $3p_x(2^2A')$ bands should have been perpendicularly polarized.

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After Paper I was published in 1998, two other studies on the electronic spectrum of H_2COH have appeared—one experimental and one theoretical. Unfortunately, both overlooked our previous report.

In the first study,[7] Aristov, Conroy, and Reisler (ACR) analyzed the rotational contours of vibronic bands related to the 3p band at $T_0 = 5.09$ eV, as obtained with (1 + 1) and (2 + 1) REMPI experiments. The $\pi^* \rightarrow 3p$ transition moment was determined to be of A' symmetry so that the upper state corresponds to $3p_z(2^2A'')$, i.e, a parallel-polarized transition. Thus, our reassignment of the high-energy band was fully confirmed by ACR's experiments.

The second article,[8] by Chen and Davidson (CD), reported extensive ab initio calculations on the 3s,3p Rydberg spectrum of H_2COH at the equilibrium and inversion geometries, using the MELD package of programs. The adiabatic ΔE's were evaluated at a lower level (CIS).

Unexpectedly, CD's results do not support the $3p_z$ assignment for the 5.09 eV band but favor the previous one involving $3p_x$. The vertical ΔE's for 3s and $3p_x$ of H_2COH(eq) calculated with MRDCI are ca. 0.4−0.6 eV smaller than those found with MELD; for $3p_y$ and $3p_z$, the deviation is acceptable (0.2 eV). These discrepancies in ΔE's—while not exceedingly large, taking into account differences in geometries, basis sets, and calculation strategies—are, however, of major relevance for H_2COH, as pointed out by the contradictory band assignments.

Possible causes for the discrepancies in vertical ΔE's between both studies could relate to the AO basis set (ours was less flexible in the Rydberg region) and/or to the dimensions of the largest matrices diagonalized (ours were 1 order of magnitude smaller).

To clarify the situation, we have recalculated the electronic spectrum of H_2COH by expanding both the AO basis set and dimensions of the diagonalized CI spaces to match closely those handled by Chen and Davidson. The new results—to be discussed below—confirm our previous assignment of the experimental spectrum.

Technical Details

(1) Geometries and Basis Sets. Comparison of the geometrical parameters for H_2COH(eq) and H_2COH(i) from Paper I with those reported by CD reveals very minor differences (MP2 data in both cases). CD optimized the geometries of the first four Rydberg states, but at the CIS level only. On average, bond distances and angles do not differ by more than 0.04 au and 2° from those of our H_2COH(ion). Therefore, for this study we keep the geometries of Paper I and also the assumption that the H_2COH(ion) geometry is a reasonable compromise for describing the adiabatic minima of the Rydberg states of H_2COH.

In Paper I, we used a basis set (A) of predominantly valence character, with only one set of diffuse s ($\alpha = 0.041$) and p ($\alpha = 0.027$) AOs on the C atom. Such basis has been expanded here by the following diffuse functions: s/p on C ($\alpha = 0.012/0.008$) and on O ($\alpha = 0.077/0.050$), as well as one s on H ($\alpha = 0.025$). The composition of this augmented basis is comparable to that taken by CD. Both lack d-Rydberg AO's, however.

The CI expansions for H_2COH(eq) are carried out using X^2A-(π^*) GS MOs. For the inversion and Rydberg (ion) geometries, $X^2A''(\pi^*)$ as well as $1^2A'(\pi^* \rightarrow 3s)$ MOs are considered. The latter have the advantage of giving more compact CI expansions for Rydberg states than those obtained with GS MOs, which in turn results in smaller residual energies for all discarded configurations (see below). Selected calculations have been done with natural orbitals (NO).

The standard frozen-core approximation is used (i.e., no excitation from the lowest (1s) MOs and discarding complementary high-lying species). This leaves 13 valence electrons to be distributed over 77 MOs.

(2) Major Steps in the MRDCI Method. Another factor leading to the discrepancies in the theoretical results might relate to the type of total energies considered to evaluate excitation energies. Below, we discuss briefly the calculation strategy of the MRDCI method.[9,10]

The first step in the MRDCI approach, as well as in the MELD, involves the generation of a "total" CI space consisting of all single and double excitations with respect to a given number of relevant configurations ("Mains"), previously determined through test calculations. We will call E^{tot} the eigenvalue of such "total" CI space. However, these spaces usually have dimensions of a few millions, so that—to keep the computational aspect tractable—a selection of configurations is undertaken for a chosen energy selection threshold (T). All configurations that give an energy lowering larger than T with respect to the reference set of Mains are being retained. In the MRDCI method, this selection is done twice, for two different values of T; the corresponding eigenvalues are $E(T_1)$ and $E(T_2)$.

During the selection procedure, the energy contribution of each of the generated configurations is estimated via perturbation theory; the cumulative energy of the discarded configurations is designated as $\Sigma\epsilon(T_1)$ and $\Sigma\epsilon(T_2)$. To a certain extent, $\Sigma\epsilon(T_1)$ is a measure of the error associated with the truncated value $E(T_1)$,— that is, it should approximately hold that $E^{tot} \approx E'(T_1) = E(T_1) + \Sigma\epsilon(T_1)$.

When calculating the transition energy between states A and B, it is evident from the expression above that $\Delta E^{tot} = [E_B{}^{tot} - E_A{}^{tot}]$ can be reproduced satisfactorily by the truncated energy difference $\Delta E(T) = [E_B(T) - E_A(T)]$ only if the residual contributions of the discarded configurations are of similar magnitude for both states.

In the MRDCI method, E^{tot} is approximated by the so-called extrapolated energy, E_{extrap}, which is obtained by adding to $E(T)$ a scaled $\Sigma\epsilon(T)$ contribution, that is

$$E_{extrap} = E(T) + \lambda\Sigma\epsilon(T)$$

The scaling factor λ is determined by using the information from the two truncated calculations at T_1 and T_2, namely

$$\lambda = [E(T_2) - E(T_1)]/[\Sigma\epsilon(T_1) - \Sigma\epsilon(T_2)]$$

Thus, in the MRDCI method, the energy of the total generated CI space (~10^6 dimension) is estimated by solving smaller CI spaces (10^4−10^5) and by extrapolating to the "total" CI space. The estimated full CI energy, E_{FCI}, is further obtained by adding to E_{extrap} the corresponding correction (FCI_{corr}) for higher excitation classes not included in the total generated CI spaces. The multireference version[10,11] of the Langhoff−Davidson correction formula[12] is

$$FCI_{corr} = (1 - \Sigma c^2)\Delta E_{MRD-CI}$$

where the sum runs over all Mains in the largest diagonalized matrix and ΔE_{MRD-CI} is the difference between E_{extra} and E_{ref}, the energy of the reference space.

According to previous experience,[10,11,13] excitation energies calculated using E_{extrap} differ little from those using E_{FCI} if the

TABLE 1: Total (hartree) and Relative (eV) Energies for the X^2A'', $1^2A'$, and $2^2A''$ States of H_2COH at the H_2COH(ion) Geometry[a]

		$E(T_1)$ ($E'(T_1)$)	$\Delta E(T_1)$ ($\Delta E'(T_1)$)	$E(T_2)$ ($E'(T_2)$)	$\Delta E(T_2)$ ($\Delta E'(T_2)$)	E_{extrap}	ΔE_{extrap}	E_{FCI}[b]	ΔE_{FCI}
$X^2A''(\pi^*)$	GS	0.77723	0.00	0.78170	0.00	0.78344	0.00	0.81219	0.00
	MOs[c]	(0.78471)	(0.00)	(0.78379)	(0.00)			[91.47%]	
	3s	0.76580	0.00	0.76997	0.00	0.77479	0.00	0.81030	0.00
	MOs[d]	(0.77619)	(0.00)	(0.77554)	(0.00)			[90.11%]	
$1^2A'(3s)$	GS	0.61906	4.30	0.62923	4.15	0.66642	3.18	0.70383	2.95
	MOs[e]	(0.68577)	(2.69)	(0.68162)	(2.78)			[89.81%]	
	3s	0.67430	2.49	0.67789	2.51	0.68024	2.57	0.70964	2.74
	MOs[f]	(0.68101)	(2.59)	(0.68054)	(2.58)			[91.21%]	
$2^2A''(3p_z)$	GS	0.60114	4.79	0.60792	4.73	0.61250	4.65	0.64751	4.48
	MOs[c]	(0.61458)	(4.63)	(0.61334)	(4.64)			[90.13%]	
	3s	0.60423	4.40	0.61176	4.30	0.61659	4.30	0.64472	4.51
	MOs[d]	(0.62119)	(4.22)	(0.61839)	(4.28)			[91.46%]	
$X^2A''(\pi^*)$	GS	0.78434	0.00	0.78578	0.00	0.78684	0.00	0.81654	0.00
	NOs[g]	(0.78480)	(0.00)	(0.78598)	(0.00)			[91.30%]	
$1^2A'(3s)$	3s	0.68640	2.67	0.68733	2.68	0.68786	2.69	0.71516	2.76
	NOs[h]	(0.68689)	(2.66)	(0.68751)	(2.68)			[91.55%]	

[a] Total energy corresponds to −114 Hartrees. The different energies are defined in the text. [b] Relative weight (in percent) of the reference configurations in the largest diagonalized CI space given in brackets. [c] 15M2R (15 mains, 2 roots)/total SAFs: 2 671 069/selected:126 884 [$T_1 = 0.4\ \mu$H]; 189 479 [$T_2 = 0.1\ \mu$H]. [d] 20M2R/3415 504/188 702 [0.3]; 265 867 [0.1]. [e] 25M3R/3507 742/198 757 [0.7]; 251 467 [0.5]. [f] 23M3R/3035 601/222 617 [0.3]; 282 607 [0.1]. [g] 14M1R/2210 497/104 346 [0.01]; 156 525 [0.0025]. [h] 16M1R/2071 569/140 645 [0.01]; 200 521 [0.0025].

weight of the reference space in the largest diagonalized matrix, Σc^2, is similarly high ($\geq$0.90) for both lower and upper state.

Knowles et al.[13] have found that E_{FCI}'s estimated according to this strategy lie very close to the exact values: a comparison of their E_{FCI}'s with exact full CI energies for 66 cases indicated a root-mean-square deviation of 0.94 kcal mol^{-1} (0.04 eV).

Results and Discussion

(1) Truncated versus Extrapolated Energies. Table 1 lists total and relative energies for the $X^2A''(\pi^*)$, $1^2A'(3s)$, and $2^2A''(3p_z)$ states of H_2COH, as calculated at the H_2COH(ion) geometry. Analysis of these data will show that internally consistent results can only be obtained after extrapolation techniques and FCI corrections are applied to truncated CI expansions.

The data tabulated are as follows: (1) values of (truncated) $E(T)$ and $\Delta E(T)$ for two selection thresholds, $T_1 > T_2$; (2) $E'(T)$ and $\Delta E'(T)$, where $E'(T) = E(T) + \Sigma\epsilon(T)$ (they are given in parentheses); (3) E_{extrap} and ΔE_{extrap}; and (4) E_{FCI} and ΔE_{FCI}. Each state has been calculated twice, using GS and 3s MOs. Also, more sophisticated calculations were undertaken for X^2A'' and $1^2A'$, using parent NOs.

Technical details are given in various footnotes to Table 1. The dimension of the total CI spaces generated ranges from 2.7 to 3.5 × 10^6 SAF's (symmetry-adapted functions), while the actually solved secular equations, for the smallest threshold T_2, lie in the 1.9−2.8 × 10^5 range. They are 1 order of magnitude larger than those handled in Paper I and slightly larger than those reported by CD.

The selection of configurations in the MO calculations has been carried out with respect to two $^2A''$ and three $^2A'$ states (roots). In other words, any of the selected CI spaces is actually a composite of a few smaller CI spaces, each related to one of the two (or three) selected roots. That is not the case for the NO calculations, where just one state has been selected, i.e., the energy lowerings are smaller, so that $E_{extrap} \approx E'(T) \approx E(T)$, and similarly for ΔE values.

As seen in Table 1, the corrected $E'(T)$ values for X^2A'' and $2^2A''$ lie about 2−17 millihartree (mH) below the corresponding $E(T)$'s. (As expected, energy lowerings $\Sigma\epsilon(T)$ are smaller for the smallest threshold T_2.) A common characteristic for a given state is that the magnitude of the difference between the corrected eigenvalues at T_2 and T_1, $E'(T_2) - E'(T_1)$, is always smaller than $|E(T_2) - E(T_1)|$, the corresponding eigenvalues difference, by about 1.5 versus 4.9 mH, respectively. In brief, the $E'(T)$ data fluctuate much less than do $E(T)$.

The study of $1^2A'(3s)$ using GS MOs represents a rather sensitive case, since the magnitude of the energy lowerings $\Sigma\epsilon(T)$ is much larger, in the 50−60 mH range. As a consequence, $\Delta E(T_2) = 4.15$ eV differs from the corrected value $\Delta E'(T_2)$ of 2.78 eV by ~1.4 eV. This feature indicates, when using GS MOs, that the truncated expansions for $1^2A'(3s)$ are less accurate than those for X^2A''. The main reason for this is that the Rydberg MOs generated in the GS SCF step are highly mixed, resulting in too many interacting configurations at the CI level. Such an unbalanced treatment for $1^2A'(3s)$, however, can be overcome by extrapolating $E(T)$ to $T = 0$, leading to $\Delta E_{extrap}(3s) = 3.18$ eV. This excitation energy is indeed significantly smaller than the directly calculated $\Delta E(T_2)$ value of 4.15 eV. The question then arises about the reliability of such a low $\Delta E_{extrap}(3s)$.

To have a reference point for comparison, complementary calculations on $X^2A''(\pi^*)$ and $1^2A'(3s)$ were carried out with 3s MOs. Now, $\Delta E_{extrap}(3s) = 2.57$ eV, even lower than using GS MOs. The truncated $1^2A'(3s)$ wave function is more compact than that generated with GS MOs, as pointed out by an energy lowering at T_2 of about 2 versus 53 mH with GS MOs. In addition, using 3s MOs, the directly calculated $\Delta E(T) \approx 2.50$ eV lies close to the corrected energy difference $\Delta E'(T) \approx 2.75$ eV obtained with GS MOs.

The calculations with parent NOs for X^2A'' and $1^2A'$ also support the E_{extrap} data obtained with both MO bases. First, it should be noted the NO results are very stable. For instance, the energy lowerings are rather low (<0.5 mH), and accordingly, E_{extrap} values lie quite close to the $E(T_2)$'s. An $\Delta E_{extrap}(1^2A') = 2.57$ eV with 3s MOs is nicely reproduced by 2.69 eV with NOs.

The data for $2^2A''(3p_z)$ are less sensitive to the treatment and/or MO basis used. Since there are only three Rydberg MOs of $a''(p_z)$ type but 12 of $a'(s,p_x,p_y)$ symmetry, the mixing between Rydberg a'' MOs is not as strong as between those of a' type.

The excitation energies at the ΔE_{FCI} level are even more independent of the treatment, as expected. For example, the

TABLE 2: Vertical Excitation Energies (in eV) for $H_2COH(eq)$, Using Ground State MOs. [a,b]

state	$\Delta E(T_1)$	$\Delta E(T_2)$	ΔE_{extrap}	ΔE_{FCI}	ΔE_{FCI} (Paper I)[c]	ΔE (CD)[d]	ΔE (Rettrup)[e]
X^2A(π^*)[f]	0.00 (0.79234)	0.00 (0.79510)	0.00 (0.79710)	0.00 (0.82690)[g]	0.00 (0.82301)	0.00 (0.72284)	0.00
2^2A(3s)[h]	4.76	4.66	4.14	3.92 [0.0090]	4.12 [0.0085]	4.71 [0.0117]	4.30 [0.0109]
3^2A($3p_x$)[h]	5.57	5.48	5.03	4.82 [0.0122]	5.05 [0.0100]	5.46 [0.0135]	5.09 [0.0171]
4^2A($3p_y$)[i]	6.45	6.34	5.58	5.40 [0.0015]	5.60 [0.0026]	5.82 [0.0010]	5.58 [0.0020]
5^2A($3p_z$)[i]	6.58	6.48	5.69	5.51 [0.0116]	5.82 [0.0130]	5.98 [0.0142]	5.65 [0.0164]
6^2A(4s)[k]	8.91	8.50	6.45	6.25 [0.0006]			
7^2A($3d_{x^2}$?)[k]	9.15	8.74	6.66	6.44 [0.0034]			
8^2A($4p_x$)[k]	9.23	8.83	6.91	6.72 [0.0005]			
9^2A($4p_z$)[k]	9.36	8.95	6.98	6.75 [0.0034]			

[a] In parentheses, total GS energy, corresponding to −114 Hartrees.[b] In brackets, oscillator strengths (f values). [c] Ref 1. [d] Ref 8. [e] Rettrup et al., ref 2. [f] 36M1R (36 mains, 1 root)/total SAFs: 8018 389/selected:140 608 [$T_1 = 0.2\ \mu$H]; 165 660 [$T_2 = 0.1\ \mu$H]. [g] E_{FCI}(GS NOs): −114.83249 H. [h] 36M2R/8018 389/199 313 [0.4]; 247 724 [0.25]. [i] 36M3R/8018 389/212 542 [0.8]; 252 443 [0.6]. [k] 36M7R/8018 389/152 718 [3.5]; 206 280 [2.5].

ΔE_{FCI} values for $2^2A''(3p_z)$ are 4.48 and 4.51 eV (GS and 3s MOs). Also, the ΔE_{FCI}'s for $1^2A'(3s)$ are 2.95, 2.74, and 2.76 eV (GS and 3s MOs, and 3s NOs). An $\Delta E_{FCI} = 2.95$ eV with GS MOs seems a little bit too high, but taking into account the relatively large overestimation errors of ΔE(T), the final result is acceptable.

The different ΔE data are diagrammatically shown in Figure 1, including the $3p_x(2^2A')$ and $3p_y(3^2A')$ states. This figure clearly shows that $\Delta E(T)$'s with GS MOs overestimate the extrapolated values by a large amount. That is not the case, however, when the 3s MO basis is used. Now, the jump between the "less accurate" value, $\Delta E(T_1)$, and the "most sophisticated" one, ΔE_{FCI}, is indeed very small.

(2) Vertical Excitation Energies for $H_2COH(eq)$. Table 2 summarizes the present vertical excitation energies, as well as those from previous ab initio studies. Excitations into selected $n = 4$ Rydberg states are reported for the first time. Here, due to the lack of symmetry, only GS MOs have been used for the CI expansions.

Analysis of the data reveals the same pattern as discussed before: truncated $\Delta E(T)$ values are substantially larger than those at the ΔE_{extrap} or ΔE_{FCI} levels. For the 3s,3p states, the discrepancies are similar to those shown in Table 1 for GS MOs. For the 4s,4p states, the extrapolation procedure similarly lowers the $\Delta E(T_2)$ values, by an average of about 2 eV. The present ΔE_{FCI} values are lower than the data reported in Paper I by only 0.2−0.3 eV. This is a very rewarding result, taking into account the much larger secular equations solved here.

Most importantly, $\Delta E(T_2)$ values of 4.66 eV for 3s and of 5.48 eV for $3p_x$ are practically the same as those reported by Chen and Davidson (4.71 and 5.46 eV). However, as seen in Table 2, the extrapolated and estimated FCI excitation energies are from 0.4 to 0.7 eV lower than those obtained with truncated CI spaces.

On the other hand, our $\Delta E(T)$ data for the $3p_y$ and $3p_z$ states are somewhat higher than those reported by CD, but again, the corresponding ΔE_{extrap} and ΔE_{FCI} results are ca. 0.2 to 0.4 eV lower than CD's values.

The ΔE's reported by Rettrup et al.[2] are slightly higher than ours but lower than CD's.

The f values are in good agreement among the different calculations: transitions into both $3p_x$ and $3p_z$ are strong, followed by 3s (intermediate) and $3p_y$ (rather weak).

TABLE 3: Excitation Energies (in eV) for H_2COH at The $H_2COH(i)$ Geometry, Using 3s MOs[a]

	$H_2COH(i)$		
state	ΔE_{FCI} (TW)	ΔE_{FCI} (Paper I)[b]	ΔE (CD)[c]
X^2A''(π^*)	0.04	0.03	0.00
$1^2A'$(3s)	3.62	3.53	4.42
$2^2A'$($3p_x$)	4.54	4.43	5.18
$3^2A'$($3p_y$)	5.11	5.11	5.60
$2^2A''$($3p_z$)	5.27	5.37	5.76
$4^2A'$(4s)	5.93		
$5^2A'$($3d_{x^2}$?)	6.17		
$6^2A'$($4p_x$)	6.31		
$3^2A''$($4p_z$)	6.61		

[a] The reference state is X^2A of $H_2COH(eq)$. [b] Ref 1. [c] Ref 8.

(3) Relative Excitation Energies for $H_2COH(i)$. The transition energies at the ΔE_{FCI} level for the Rydberg states of $H_2COH(i)$, calculated with 3s MOs, are reported in Table 3. The orders of the CI spaces diagonalized are similar to those reported in Table 1. Our ΔE's are relative to the energy of the X^2A ground state at the $H_2COH(eq)$ geometry, using GS MOs.

As known from previous studies (see extended bibliography in ref 4), the inversion barrier for GS H_2COH is very small. The present value of 0.04 eV is in line with expectations. As seen in Table 3, the new excitation energies for $H_2COH(i)$ agree within ±0.1 eV with those reported in Paper I (ΔE_{FCI} data as well, but using GS MOs and diagonalizing smaller matrices). However, they are lower than the values given in CD's work (by about 0.8 eV for 3s, and 0.5 to 0.6 eV for 3p), which were obtained for a $H_2COH(i)$ geometry similar to ours. As discussed earlier, excitation energies derived from truncated CI spaces and GS MOs overestimate the corresponding extrapolated and/or full CI values.

(4) Adiabatic Excitation Energies for the $H_2COH(ion)$ Geometry. Adiabatic excitation energies, ΔE_{FCI}, are shown in Table 4. The electronic second moments at the $H_2COH(ion)$ geometry are also given; this information helps to determine the structure of Rydberg states by simple inspection.

At the $H_2COH(ion)$ geometry, the GS lies 0.43 eV higher (0.45 eV, Paper I). Again, the new excitation energies for 3s,3p lie close to those reported earlier, with an average deviation of 0.05 eV between both sets of data.

TABLE 4: Electronic Second Moments[a](au) and Adiabatic Excitation Energies (in eV) for H_2COH at the H_2COH(ion) Geometry, Using 3s MOs[a]

state	$-\langle x^2\rangle$	$-\langle y^2\rangle$	$-\langle z^2\rangle$	ΔE_{FCI} (TW)	ΔE_{FCI} (Paper I)[b]	ΔE_{CIS}[c] (CD)[d]	T_0[e] (TW)	T_0 exptl.
X^2A'' (π^*)	8.5	7.5	11.2	0.43	0.45			
$1^2A'$(3s)	18.1	20.6	16.7	3.17	3.23	4.12	3.31	
$2^2A'$ $(3p_x)$	28.4	20.6	20.4	4.27	4.09	5.20	4.41	4.34[f]
$3^2A'$ $(3p_y)$	25.4	39.6	23.0	4.75	5.04	5.72	4.89	
$2^2A''$ $(3p_z)$	21.0	21.7	57.0	4.92	5.06	5.8	5.06	5.09[g]
$4^2A'$(4s)	53.8	48.2	41.7	5.54			5.68	
$5^2A'$ $(3d_{x^2}?)$	52.7	35.4	27.9	5.77			5.91	
$6^2A'$ $(4p_x)$	82.6	50.3	44.1	6.01			6.15	
$3^2A''$ $(4p_z)$	39.9	40.7	114.2	6.26			6.40	

[a] The reference energy for our data is X^2A or H_2COH(eq). Electronic moments $\langle x^2\rangle$, $\langle y^2\rangle$, and $\langle z^2\rangle$ with the C atom at the origin of coordinates. [b] Ref 1. [c] Ground and excited states geometries optimized at the CIS level. [d] Ref 8. [e] Estimated using $\Delta ZPE = 0.14$. [f] Ref 3. Assigned by us to $\pi^* \rightarrow 3p_x$ $(2^2A')$, CO-perpendicular polarization (Paper I and TW). [g] Refs 3−5 and 7. Assigned by us to $\pi^* \rightarrow 3p_z$ $(2^2A'')$, CO-parallel polarization (Paper I and TW); confirmed experimentally, ref 7.

CD carried out CIS calculations for the $n = 3$ Rydberg states at their corresponding equilibrium geometries. The adiabatic CIS transition energies are about 1 eV higher than our FCI values (Table 4). CIS studies on the Rydberg transitions of H_2CO and $(CH_3)_2CO$ are affected by similarly large errors.[14]

The electronic second moments show clearly the Rydberg character of 3s to $4p_z$, with increasing diffussenes between $n = 3$ and $n = 4$, and a dominance of $\langle x^2\rangle$, $\langle y^2\rangle$, and $\langle z^2\rangle$ for p_x, p_y, and p_z, respectively.

As seen in Tables 2−4, all theoretical studies agree in the ordering $3p_x < 3p_y < 3p_z$ for the 3p Rydberg states (the main difference lies in our excitation energies being lower).

The situation for 4s,4p is more complicated. Our calculations on the higher Rydberg states missed the $4p_y$ component but found instead an additional diffuse state (the seventh ^2A for H_2COH(eq) in Table 2, or the fifth $^2A'$ for H_2COH(i) and H_2COH(ion) in Tables 3 and 4). From the $\langle r^2\rangle$ data in Table 4, the best assignment involves the occupation of the (nonoptimal) $3d_{x^2}$ orbital in the upper state.

(5) Confirmation of our Previous Assignment. According to Paper I and ref 4, the ZPE of H_2COH^+ is about 0.14 eV larger than that for H_2COH(eq), both in their GS's. Assuming the same ΔZPE correction for all Rydberg states, the adiabatic ΔE_{FCI}'s in Table 4 have been increased by 0.14 eV to get approximate T_0 values.

A calculated $T_0 = 3.31$ eV for the first excited state, $\pi^* \rightarrow 3s$, is 1 eV smaller than the lowest excitation energy experimentally detected so far ($T_0 = 4.34$ eV). On the other hand, a calculated $T_0 = 4.41$ eV for the next state, $\pi^* \rightarrow 3p_x$, reproduces nicely the experimental result.

Excitations into $3p_y$ and $3p_z$ are predicted to have T_0's of 4.89 and 5.06 eV, respectively. Energetically, both could be possible carriers of an experimental band progression starting at $T_0 = 5.09$ eV. However, calculated oscillator strengths indicate that the transition into $3p_y$ is extremely weak, whereas that into $3p_z$ is relatively strong (Table 2). Thus, the high-energy absorption band relates to the excitation $\pi^* \rightarrow 3p_z$ $(2^2A'' \leftarrow X^2A'')$, as found in Paper I and in REMPI experiments.[7]

Summary and Conclusions

The electronic spectrum of H_2COH has been reinvestigated using expanded AO basis sets and large CI spaces. This study has been prompted by a recent article published in this Journal by Chen and Davidson, whose calculations support transitions from π^* into 3s (lower) and $3p_x$ (upper) for the two currently known absorption bands of H_2COH, as was also postulated by Rettrup et al. a few years ago. On the other hand, our earlier study—published before CD's—assigned a different character to the excited states, namely $3p_x$ (lower) and $3p_z$ (upper).

Here, we have carried out new CI calculations following closely the technical conditions used by CD regarding quality of the AO basis set and dimensions of the diagonalized matrices. The MRDCI approach, however, goes further by extrapolating energies to the total generated CI spaces and applying a full CI correction thereafter.

The present results confirm our previous assignment: experimental T_0 values of 4.34 and 5.09 eV correspond to $\pi^* \rightarrow 3p_x$ and $\pi^* \rightarrow 3p_z$, respectively ($T_0 \approx 4.41$ and 5.06 eV, this work). A CO-parallel polarization predicted for the $\pi^* \rightarrow 3p_z$ band has been confirmed experimentally.[7]

The main cause for the discrepancy between our ΔE's and those reported by CD lies in their use of directly diagonalized (and not extrapolated) energy eigenvalues, which lead to vertical ΔE's being 0.5−0.8 eV higher than those obtained using extrapolated or estimated full CI results. In addition, in ref 8, adjustments for the change in geometry between GS and Rydberg states, and corresponding zero-point energy corrections, had not been made at the multireference CI level.[15]

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