

Cluster expansion of the wave function. Electron correlations in the ground state, valence and Rydberg excited states, ionized states, and electron attached states of formaldehyde by SAC and SAC-CI theories

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The SAC (symmetry-adapted-cluster) and SAC-CI theories are applied to the study of electron correlations in the ground state, valence and Rydberg excited states, ionized states, and electron attached states of formaldehyde. The results compare well with experiments, showing the utility of the SAC and SAC-CI theories. Some new assignments of the spectra are reported.

I. INTRODUCTION

In this series of studies we are developing cluster expansion theories not only for closed shell ground states but also for open shell and excited states, ionized states, and electron attached states.¹⁻⁶ The SAC (symmetry-adapted-cluster) theory was developed for closed and open shell ground states¹ and recently extended to excited states.⁶ SAC-CI theory was developed for excited states, ionized states, and electron attached states.^{3,4} It utilizes the fact that the subspace of the SAC ground state spans an adequate basis for excited states, ionized states, and electron attached states. Physically, this means that the electron correlation in the ground state gives a good starting point for the study of electron correlations in these excited states. In the cluster expansion formalism, Paldus *et al.*,⁷ Lindgren,⁸ and Ohmine⁹ have also given interesting approaches to open shell and excited states.

We have given the theories for the SAC and SAC-CI expansions in previous papers.^{1,3} Formulations for actual applications (programming) of the theories were summarized in two previous papers.^{4,5} Applications were given for some simple systems (Be, BH₃, and H₂O) with the first version of the program.⁴ The results were excellent in comparison with the full or nearly full CI results for both ground and singlet excited states. More systematic applications to H₂O for the ground state, singlet and triplet excited states, ionized states, and electron attached states were given previously with the use of the second version of the program.⁵ The results showed satisfactory agreements with experiments. Applications of the SAC theory to excited states were reported for Be, H₂O, and CH₂ with excellent agreement with experiment.⁶ For excited states, the SAC-CI theory is easier and less time consuming than the SAC theory, though the latter will give more accurate results.

In this paper, we apply the SAC and SAC-CI theories to formaldehyde. Formaldehyde is a molecule for which spectroscopic studies are widely reported from both experimental¹⁰⁻¹⁴ and theoretical¹⁵⁻²⁵ works. The experi-

mental aspects of the excited states were reviewed in detail by Moule and Walsh.¹⁰ The valence and Rydberg excitations and the mixing thereof are of interest.¹⁵⁻²² The photoelectron spectra are well studied^{12,13} and different assignments were made by different theories.²⁴ The nature of the electron attached states^{11,14} still seems uncertain. Formaldehyde thus includes chemical complexities well and yet is very small, so that it is a good subject for testing of new theories. We calculate here the ground state by the SAC theory.¹ Singlet and triplet excited states, ionized states, and electron attached states are calculated by the SAC-CI theory.³ As excited states we study both valence and Rydberg states, and a mixing thereof (especially for the singlet $\pi \rightarrow \pi^*$ state). The computational scheme used here is the same as the one used previously for H₂O.⁵

II. CALCULATIONAL DETAILS

A. Basis sets and geometry

Two kinds of basis sets were used in order to study mixing between valence and Rydberg excited states. One is the double zeta [3s2p/2s] CGTO's of Huzinaga²⁶ and Dunning²⁷ (valence only basis). The other includes a valence basis plus Rydberg basis (single GTO's with exponents 0.023 and 0.021 for 3s and 3p AO's, respectively, of carbon and 0.032 and 0.028 for 3s and 3p AO's, respectively, of oxygen).²⁷ This basis is denoted the valence and Rydberg basis. The experimental geometry²⁸ $R_{CO} = 1.2099 \text{ \AA}$, $R_{CH} = 1.1199 \text{ \AA}$, and $\angle HCH = 118^\circ$ was used for all calculations. The molecule lies on the yz plane with the z axis parallel to the CO bond.

B. Computational method

The ground state was calculated by the SAC expansion around the Hartree-Fock reference state $|0\rangle$:

$$\Psi_e = \exp\left(\sum_I C_I S_I^+\right) |0\rangle, \quad (1)$$

where S_I^+ is a symmetry-adapted (singlet c_i) excitation operator. The expansion was terminated at second order in the coefficients

$$\Psi_e \approx \left[1 + \sum_I C_I S_I^\dagger + \left(\frac{1}{2} \right) \sum_{I,J} C_I C_J S_I^\dagger S_J^\dagger \right] |0\rangle. \quad (2)$$

As linked configurations $S_I^\dagger |0\rangle$, we have included all single and double excitations from the reference $|0\rangle$. In the unlinked configurations $S_I^\dagger S_J^\dagger |0\rangle$, we have included quadruple excitations as products of double excitations. It takes account of the "simultaneous collisions" of electrons in different spaces of molecules.²⁹ For the closed shell ground state, double and triple excitations in the unlinked terms can be neglected.^{29,30} For practical reasons, the double excitations included in the unlinked terms $S_I^\dagger S_J^\dagger |0\rangle$ were those which have coefficients larger than 10^{-3} in the CI expansion including all single and double excitations. Of the two methods of solving the SAC equation (variational and nonvariational),³ we have used only the nonvariational (SAC-MET) method.

The excited states (singlet and triplet), ionized states, and electron attached states were studied by the SAC-CI expansion³

$$\Psi_e = \sum_K d_K \Phi_K, \quad (3)$$

$$\Phi_K = \mathcal{O} R_K^* \Psi_e,$$

where d_K is an expansion coefficient. The excited function Φ_K is formed from the SAC ground state Ψ_e by operating an excitation, ionization, or electron attachment operator R_K^* , which is symmetry adapted. \mathcal{O} is a projection operator $\mathcal{O} = 1 - |\Psi_e\rangle\langle\Psi_e|$. It was shown that the excited functions $\{\Phi_K\}$ thus formed span an excellent configuration space for the excited states.³ Here, we have terminated the expansion at the second order in the coefficients

$$\Psi_e = \sum_K d_K \left(R_K^* + R_K^* \sum_I C_I S_I^\dagger - s_{K\epsilon} \right) |0\rangle, \quad (4)$$

where $s_{K\epsilon} = \langle\Psi_e | R_K^* \Psi_e\rangle$. As linked configurations $R_K^* |0\rangle$, we have included all single and double excitations from the reference Hartree-Fock configuration $|0\rangle$ of the closed shell ground state. For the unlinked configurations $R_K^* \sum_I C_I S_I^\dagger |0\rangle$, we have used the following simplifications: Since the excited, ionized, and electron attached states studied here are primarily of single excitation in nature, we have included only the single excitation operators for the R_K^* . Since the SAC coefficients C_I of the ground state are large only for double excitations, the operators S_I^\dagger included are the double excitations whose coefficients are larger than 10^{-3} in the CI including all single and double excitations. The unlinked terms thus include double excitations from all singly excited configurations $R_K^* |0\rangle$, the coefficients C_I of the double excitations being transferred from the ground state SAC

TABLE I. Correlation energy for the ground state of formaldehyde (a. u.).

Method	Valence	Valence and Rydberg
Hartree-Fock	-113.828787	-113.830934
(1+2) CI	-0.204616	-0.206097
SAC-MET	-0.220291	-0.220293

TABLE II. Vertical excitation energy of formaldehyde calculated with the valence only basis (eV).^a

State	Orbital picture	SAC-CI-V	SAC-CI-NV	Exptl. ^b
³ A ₂	$n \rightarrow \pi^*$	3.69	3.72	3.5, 3.3-3.6
¹ A ₂		4.17	4.19	4.1, 4.2
³ A ₁	$\pi \rightarrow \pi^*$	6.09	6.10	6.0, 5.6-6.2
¹ A ₁		10.87	10.90	10.7

^aRelative to the ground state energy of -114.049078 a. u.

^bReferences 20 and 22.

calculations. Since for the most part the correlations in the excited, ionized, and electron attached states should be similar to those of the ground state, this approximation should be reasonable. The SAC-CI method includes the idea of multireference CI³¹ in this way.

The SAC-CI wave function was solved by the variational (SAC-CI-V) and nonvariational (SAC-CI-NV) methods.³ The former involves a symmetric matrix and the latter a nonsymmetric matrix. Davidson's algorithm³² was used for a diagonalization of the symmetric matrix. For the nonsymmetric matrix we have extended Davidson's algorithm. Details will be published elsewhere.³³

III. GROUND STATE, VALENCE, AND RYDBERG EXCITED STATES OF FORMALDEHYDE

We have used two kinds of basis set, i. e., valence only basis and valence and Rydberg basis, in order to study the nature of excited states. In Table I we have summarized the correlation energies obtained for the ground state of formaldehyde. The effect of "simultaneous collisions" of electrons as products of pair excitations included in the SAC-MET theory lowers the energy by about 0.015 a. u. in comparison with the CI including all single and double excitations (1+2) CI. The effect of Rydberg orbitals on the ground state energy is negligibly small, as expected.

Table II shows vertical excitation energies calculated with the valence only basis. Table III shows those calculated with the valence and Rydberg basis. ^{1,3}($n \rightarrow \pi^*$) excitations and ³($\pi \rightarrow \pi^*$) excitation are well established to be valence transitions so that the results obtained by the valence only basis agree well with experiment. For the ¹($\pi \rightarrow \pi^*$) transition there have been long controversies whether it is a valence-like transition or a Rydberg-like transition.¹⁵⁻²² Experimental determination seems difficult since no experimental evidence for the ¹($\pi \rightarrow \pi^*$) transition could be found in either the absorption or the electron scattering spectra.¹⁰ (The value 10.7 eV in Tables II and III is due to the unpublished spectra of A. Chutjian assigned by Harding and Goddard.²²) Theoretically, recent large scale CI calculations tend to assign it as mostly valence.^{16,19,22} For example, Harding and Goddard²² concluded that the ¹($\pi \rightarrow \pi^*$) state is essentially (~90%) valence in character. In the present study we see that the calculations including the valence basis alone (Table II) already give a reasonable agreement

TABLE III. Vertical excitation energy of formaldehyde for valence and Rydberg excitations (eV).

State	Orbital picture	SAC-CI ^a		Exptl. ^b	YM, ^c EOM	LD, ^c CI	HG, ^c GVB-CI
		V	NV				
³ A ₂	<i>n</i> → <i>π</i> *	3.67	3.70	3.5, 3.3–3.6	3.46	3.70	3.68
¹ A ₂		4.13	4.16	4.1, 4.2	4.04	4.07	4.09
³ A ₁	<i>π</i> → <i>π</i> *	6.08	6.10	6.0, 5.6–6.2	5.29	6.21	5.95
¹ A ₁		10.80	10.83	10.7	10.10	11.05	10.77
³ B ₂	<i>n</i> → 3 <i>s</i>	6.84	6.92	7.09, 6.7–7.0	...	6.94	7.08
¹ B ₂		6.99	7.07	7.091, 7.13	7.28	7.10	7.16
³ B ₂	<i>n</i> → 3 <i>p_z</i>	7.76	7.83	7.92			7.99
¹ B ₂		7.91	7.99	7.97, 8.00			8.08
³ A ₁	<i>n</i> → 3 <i>p_y</i>	7.85	7.92	8.11	...	7.81	8.05
¹ A ₁		7.92	8.00	8.14	8.15	7.86	8.09
³ A ₂	<i>n</i> → 3 <i>p_x</i>	8.14	8.22				8.31
¹ A ₂		8.13	8.20				8.32
³ B ₁	5 <i>a</i> ₁ (<i>σ</i>) → <i>π</i> *	8.49	8.52	8.50 ^d			
¹ B ₁		9.46	9.49	9.0	9.19	9.30	
³ A ₂	1 <i>b</i> ₂ (<i>σ</i>) → <i>π</i> *	10.78	10.80				
¹ A ₂		11.17	11.19				
³ B ₁	<i>π</i> → 3 <i>s</i>	11.03	11.06			11.27	10.68
¹ B ₁		11.13	11.16	10.7	11.2	11.29	10.73
³ B ₁	<i>π</i> → 3 <i>p_z</i>	11.94	11.98				11.57
¹ B ₁		12.12	12.16	11.6–11.9	12.2		11.66

^aCalculated with the valence and Rydberg basis. Excitation energies are relative to the ground state energy of -114.051227 a. u.

^bReferences 20 and 22.

^cYM: Yeager-McKoy (Ref. 18). LD: Langhoff-Davidson (Ref. 20). HG: Harding-Goddard (Ref. 22).

^dReference 11.

with experiment. Comparing Tables II and III, we see further that the effects of the Rydberg basis on the excitation energies are very small not only for the ^{1,3}(*n* → *π**) and ³(*π* → *π**) transitions but also for the ¹(*π* → *π**) transition. This shows that the ¹(*π* → *π**) state is essentially valence in character, at least when it is viewed from the excitation energy.

In order to examine this problem further from a different point of view, we have shown in Table IV the dipole moments and second moments of the ground and excited states calculated with the valence only basis and with the valence and Rydberg basis. The second moment gives a measure of the size of the electron cloud. It is seen that the calculated dipole moments for the ground and *n* → *π** excited states show fair agreements with experiments, though for excited states the geometry used is

different from the experimental one.¹⁰ For the ^{1,3}(*n* → *π**) and ³(*π* → *π**) states the second moments are typically those of the valence states (compared with the ground state values) and the effects of the Rydberg basis are very small. For the ¹(*π* → *π**) state, however, both of the dipole moment and second moment are affected largely by the addition of the Rydberg basis set. It shows that, though the excitation energy is insensitive to the Rydberg basis, the wave function itself is not and includes Rydberg nature to some extent. Since the dipole moment changes largely from 0.81 a. u. (2.1 D) to 0.59 a. u. (1.5 D), experimental observation should be very useful. We conclude that the ¹(*π* → *π**) state has a small Rydberg character when it is measured by the dipole moment and second moment.

Table III summarizes the present results for the ver-

TABLE IV. Dipole moment and second moment of formaldehyde (a. u.).^a

State	Orbital picture	Valence only basis				Valence and Rydberg basis				Exptl. ⟨ <i>z</i> ⟩
		⟨ <i>z</i> ⟩	⟨ <i>x</i> ² ⟩	⟨ <i>y</i> ² ⟩	⟨ <i>z</i> ² ⟩	⟨ <i>z</i> ⟩	⟨ <i>x</i> ² ⟩	⟨ <i>y</i> ² ⟩	⟨ <i>z</i> ² ⟩	
¹ A ₁	ground	1.015	8.78	15.27	37.53	1.033	8.89	15.41	37.70	0.913 ^b
³ A ₂	<i>n</i> → <i>π</i> *	0.502	10.57	14.23	37.31	0.491	11.50	14.58	38.00	0.508 ^{c,e}
¹ A ₂		0.605	10.45	14.20	37.35	0.599	11.29	14.52	38.05	0.614 ^{d,e}
³ A ₁	<i>π</i> → <i>π</i> *	0.451	9.16	15.45	38.29	0.467	9.81	15.74	38.81	...
¹ A ₁		0.809	9.67	15.75	38.59	0.590	13.58	19.24	42.66	...

^aResults of SAC-CI-NV calculations. The second moment is calculated around the center of nuclear charge. The conversion factor between a. u. and D for dipole moment is 1 a. u. = 2.541770 D.

^bK. Kondo and T. Oka, J. Phys. Soc. Jpn. 15, 307 (1960).

^cA. D. Buckingham, D. A. Ramsay, and J. Tyrrell, Can. J. Phys. 48, 1242 (1970).

^dD. E. Freeman and W. Klemperer, J. Chem. Phys. 45, 52 (1966).

^eThe observed dipole moments of the *n* → *π** excited states correspond to different geometries.

TABLE V. Dipole moment and second moment of the vertical excited states of formaldehyde calculated with the valence and Rydberg basis (a. u.).^{a,b}

State	Orbital picture	Dipole moment $\langle z \rangle$	Second moment		
			$\langle x^2 \rangle$	$\langle y^2 \rangle$	$\langle z^2 \rangle$
³ B ₂	<i>n</i> → 3 <i>s</i>	-1.205	20.79	26.43	49.27
¹ B ₂		-1.184	22.18	27.14	49.97
³ B ₂	<i>n</i> → 3 <i>p_z</i>	0.744	20.39	24.69	63.24
¹ B ₂		0.237	21.48	25.73	67.36
³ A ₁	<i>n</i> → 3 <i>p_y</i>	-0.010	20.08	47.54	47.00
¹ A ₁		0.005	20.31	48.17	47.10
³ A ₂	<i>n</i> → 3 <i>p_x</i>	0.114	43.71	24.50	46.98
¹ A ₂		0.098	43.73	24.50	46.97
³ B ₁	5 <i>a</i> ₁ (<i>σ</i>) → <i>π</i> *	0.092	11.22	15.65	37.03
¹ B ₁		0.287	11.21	15.59	37.14
³ A ₂	1 <i>b</i> ₂ (<i>σ</i>) → <i>π</i> *	1.378	11.70	14.34	38.70
¹ A ₂		1.311	11.66	14.29	38.49
³ B ₁	<i>π</i> → 3 <i>s</i>	-0.987	19.66	27.49	48.85
¹ B ₁		-1.256	20.04	27.81	50.25
³ B ₁	<i>π</i> → 3 <i>p_z</i>	0.299	18.53	25.30	64.30
¹ B ₁		0.569	20.28	27.03	66.97

^aCalculated by the SAC-CI-NV method.^bFor the ^{1,3}(*n* → *π**) and ^{1,3}(*π* → *π**) states, see Table IV.

tical excitations of formaldehyde including valence and Rydberg transitions. They were calculated with the valence and Rydberg basis. The assignments of the experimental values follow those of Harding and Goddard, who used the GVB-CI method.²² The results due to Yeager and McKoy,¹⁸ who used the equation-of-motion method, and those of Langhoff and Davidson,²⁰ who used the CI method, are also cited for comparison. It is seen that the present results show satisfactory agreement with experiments and also with the results of the previous calculations.^{18,20,22} The SAC-CI-V results are consistently smaller than the SAC-CI-NV results by 0.01–0.08 eV. Van Veen, Van Dijk, and Brongersma¹¹ reported a new transition at 8.50 eV by threshold electron-impact spectroscopy of formaldehyde. From the present calculation we assign this peak to the ³B₁ [*5a*₁(*σ*) → *π**] transition, which is valence in character as will be seen in Table V.

The singlet-triplet separations in excited states of formaldehyde are grouped into three classes, as

Peyerimhoff and Buenker pointed out.¹⁶ The largest one is the in-plane transition, which is the *π* → *π** transition. The separation is as large as 4.7 eV. The smallest class includes Rydberg transitions. The calculated separations are -0.02 to 0.2 eV. An interesting one is the ^{1,3}A₂(*n* → 3*p_x*) transitions for which the singlet state was calculated a bit lower than the triplet state. The intermediate class includes intervalence excitations involving different symmetry planes like *n* → *π** and *σ* → *π** transitions. The calculated separations are 0.4 to 1.0 eV. These differences are parallel to the magnitudes of the exchange integrals between the MO's involved, though the origin of the Hund rule is not necessarily attributed to this integral.³⁴

Table V shows the dipole moments and second moments of the vertically excited states of formaldehyde (for the *n* → *π** and *π* → *π** states see Table IV). These values are obtained by the valence and Rydberg basis. Interestingly, the ^{1,3}[*5a*₁(*σ*) → *π**] and ^{1,3}[1*b*₂(*σ*) → *π**] excited states are all shown to be purely valence in nature. In comparison with Table IV, the second moments of these states are similar to those of the ^{1,3}(*n* → *π**) and ³(*π* → *π**) states. The other states in Table V are typically Rydberg in nature as seen from the second moment. For the excitation into the 3*p_α* orbital, the second moment increases in *α* direction. The dipole moment of the excited state varies largely from state to state. Especially, the dipole moments of the ^{1,3}(*n* → 3*s*) and ^{1,3}(*π* → 3*s*) states are large negative, showing shifts of electron density toward hydrogen. The singlet-triplet difference is larger in the dipole moment than in the second moment. For Rydberg excited states, the singlet state is generally a bit more diffuse than the corresponding triplet.

Table VI summarizes the results of oscillator strength for the singlet excitations of formaldehyde. They were calculated from the transition moment $\langle \mathbf{r} \rangle_{ee}$ by

$$f = (2/3) \Delta E |\langle \mathbf{r} \rangle_{ee}|^2, \quad (5)$$

with the use of the valence and Rydberg basis, except for those shown in parentheses. The present results show good agreement with experiments except for the ¹(*n* → 3*p_y*) transition. We note that for the ¹(*π* → *π**) transition the effect of the Rydberg basis is relatively large as for the dipole moment and second moment. The ¹(*n* → *π**) transition is forbidden since it belongs to the A₂

TABLE VI. Oscillator strength for singlet excitations of formaldehyde (a. u.).^{a,b}

State	Orbital picture	SAC-CI-V	SAC-CI-NV	Exptl. ^d	YM, ^d EOM	LD, ^d CI	HG, ^d GVB-CI
¹ A ₁	<i>π</i> → <i>π</i> *	0.184(0.232) ^c	0.167(0.212) ^c		0.10	0.222	0.255
¹ B ₂	<i>n</i> → 3 <i>s</i>	0.0200	0.0203	0.028	0.02	0.034	0.006
¹ B ₂	<i>n</i> → 3 <i>p_z</i>	0.0287	0.0294	0.032			0.038
¹ A ₁	<i>n</i> → 3 <i>p_y</i>	0.0402	0.0417	0.017	0.05	0.0003	0.015
¹ B ₁	5 <i>a</i> ₁ (<i>σ</i>) → <i>π</i> *	0.0048	0.0048		0.002	0.0014	
¹ A ₁	<i>n</i> → 3 <i>d_{yz}</i>	0.0192	0.0186	0.015			0.0005
¹ B ₁	<i>π</i> → 3 <i>s</i>	0.0416	0.0423			0.00057	0.026
¹ B ₁	<i>π</i> → 3 <i>p_z</i>	0.0327	0.0336				0.026

^aThe transition to the state of A₂ symmetry is forbidden.^bResults obtained with the valence and Rydberg basis.^cValues in parentheses were obtained with the valence only basis.^dYM: Yeager-McKoy (Ref. 18). LD: Langhoff-Davidson (Ref. 20). HG: Harding-Goddard (Ref. 22).

TABLE VII. Ionization potential of formaldehyde (eV).^a

State	Orbital picture	Koopmans	Δ SCF	SAC-CI-V ^b	SAC-CI-NV ^b	Exptl.
² B ₂	$n \rightarrow \infty$	12.12 ^c	9.67 ^c	10.48	10.56	10.88, ^d 10.9 ^e
² B ₁	$\pi \rightarrow \infty$	14.67	12.66	14.66	14.70	14.38, ^d 14.5 ^e
² A ₁	$5a_1 \rightarrow \infty$	17.56		15.75	15.83	15.85, ^d 16.2 ^e
² B ₂	$1b_2 \rightarrow \infty$	19.23		17.59	17.64	16.25, ^d 17.0 ^e
² A ₁	$4a_1 \rightarrow \infty$	23.65		21.77	21.81	21.15 ± 0.15 ^f

^aResults obtained with the valence and Rydberg basis.

^bRelative to the neutral ground state energy of -114.051227 a. u.

^cReference 23.

^dReference 12.

^eReference 24.

^fReference 13.

symmetry. Though the GVB-CI method²² gave excellent agreement with experiments for the transition energy, it was not so good for the oscillator strength. (The basis sets used in the GVB-CI and present calculations are similar.)

IV. IONIZED STATES AND ELECTRON ATTACHED STATES OF FORMALDEHYDE

The ionization spectrum of formaldehyde is well studied by photoelectron spectroscopy¹² and (*e*, 2*e*) experiments.¹³ There was an uncertainty in the assignments of the third and fourth ionization potentials in both experimental^{12,13} and theoretical²⁴ works, though now the assignments are well established.¹³ Table VII shows the present results of the SAC-CI theory and compares them with the experimental values. The basis set is the valence and Rydberg basis. For the first five ionization potentials, which are essentially of one electron processes, the present theory gives satisfactory agreement with experiment. The assignment of the spectra is consistent with the well established ones.¹³ The Koopmans values are consistently too large except for a coincidence in the second ionization potential. The Δ SCF values are smaller than the experimental values. This is expected since the electron correlation in the ionized state should be smaller than that in the ground state. The SAC-CI theory includes the electron correlations of both states in a balanced way. The SAC-

CI-V results are a bit smaller than the SAC-CI-NV results.

Electron transmission spectroscopy³⁵ has given the electron affinity of formaldehyde through the formation of a temporary negative ion.^{11,14} Burrow and Michejda¹⁴ and Van Veen, Van Dijk, and Brongersma¹¹ have reported electron transmission spectra at 0.66, 0.86, 1.06, 1.24, 1.41, and 1.58 eV. Burrow and Michejda assigned these peaks as being due to the vibrational levels of the ²B₁ ground state of H₂CO⁻ in which an electron is trapped in the π^* orbital. Vertical electron affinity was reported to be -0.86 eV.^{11,35}

In Table VIII we have summarized the present results for the electron affinity of formaldehyde. Table IX shows the second moments of the corresponding lower-lying electron attached states. They were calculated with the valence and Rydberg basis. Due to our calculations the first lower-lying anion states will appear about 0.7-1.2 eV above the neutral ground state. Referring to Table IX, we see that these anion states are largely of Rydberg nature. Among these, the lowest ²B₁ state calculated at 1.02-1.05 eV above the ground state is a mixture of π^* and 3*p_x* orbitals and is relatively contracted. We assign the observed peak at -0.86 eV as corresponding to this level. Though the other peaks observed in the range -0.66- -1.24 eV were reported to be the corresponding vibrational levels,¹⁴ we propose a possibility

TABLE VIII. Electron affinity of formaldehyde (eV).^a

State	Orbital picture	Koopmans	Δ SCF	SAC-CI-V ^b	SAC-CI-NV ^b	Exptl. ^c
² A ₁	$\infty \rightarrow a_1(3s)$	-0.775	-0.742	-0.702	-0.734	-0.66
² B ₁	$\infty \rightarrow b_1(\pi^*, 3p_x)$	-1.06	-1.05	-1.02	-1.05	-0.86
² B ₂	$\infty \rightarrow b_2(3p_y)$	-1.21	-1.20	-1.16	-1.19	-1.06
² A ₁	$\infty \rightarrow a_1(3p_z)$	-1.27		-1.20	-1.22	-1.24
² B ₁	$\infty \rightarrow b_1(3p_x, \pi^*)$	-2.91		-2.57	-2.60	
² A ₁	$\infty \rightarrow a_1(3p_z)$	-3.05		-2.93	-2.95	
...	
² A ₁	$\infty \rightarrow a_1(C-H^*)$	-8.22		-7.72	-7.75	

^aCalculated with the valence and Rydberg basis.

^bRelative to the neutral ground state energy of -114.051227 a. u.

^cReferences 11 and 14. See also Ref. 34.

TABLE IX. Second moment of the lower-lying electron attached states of formaldehyde (a. u.).^a

State	Orbital picture	$\langle x^2 \rangle$	$\langle y^2 \rangle$	$\langle z^2 \rangle$
² A ₁	$\infty \rightarrow a_1(3s)$	-25.71	-32.33	-70.95
² B ₁	$\infty \rightarrow b_1(\pi^*, 3p_x)$	-20.71	-20.21	-45.54
² B ₂	$\infty \rightarrow b_2(3p_y)$	-23.70	-59.69	-56.29
² A ₁	$\infty \rightarrow a_1(3p_{zC})$	-30.44	-36.95	-74.06
² B ₁	$\infty \rightarrow b_1(3p_x, \pi^*)$	-33.23	-23.84	-56.65
² A ₁	$\infty \rightarrow a_1(3p_{zO})$	-19.44	-25.95	-76.13

^aCalculated by the SAC-CI-NV method with the valence and Rydberg basis.

that they are due to the other different anion states as shown in Table VIII.

Özkan *et al.*²⁵ reported the vertical π^* electron affinity of formaldehyde to be -2.22 eV by the Δ SCF method including the valence basis alone. The present calculations with the valence only basis gave the π^* electron affinity at -2.61 eV (SAC-CI-V) and -2.63 eV (SAC-CI-NV). These results are close to the second ²B₁ states calculated with the valence and Rydberg basis. We conclude that the observed transmission spectra at around 0.86 eV are not explained without a strong participation of the Rydberg orbitals.

For the electron attachment to the Rydberg AO's, the Koopmans theorem and the Δ SCF treatment give fairly good agreement with the SAC-CI results which include fully the correlation effects in both ground and electron attached states. This is not unexpected since an electron attached in the Rydberg orbital is far apart from the valence orbitals and the interaction between them should be small. For the electron attachment in the CH antibonding orbital, the Koopmans value is less satisfactory.

V. CONCLUSION

In the present study we have seen that the SAC and SAC-CI theories have given satisfactory results for the ground state, vertically excited states, ionized states, and electron attached states of formaldehyde. In addition to the previous calculations,⁴⁻⁶ the present results show a utility of the present theory for the study of these various states. The SAC and SAC-CI theories include electron correlations in ground, excited, ionized, and electron attached states in a reasonable and balanced way. This is true for both valence and Rydberg states and for a mixed state between them. Because of the coupled cluster approach, the sizes of the matrices to be diagonalized are relatively small in both of the SAC and SAC-CI theories. Another merit is that we have used the Hartree-Fock determinant $|0\rangle$ and its MO's of the ground state throughout not only in the SAC calculations of the ground state but also in all of the SAC-CI calculations of the excited states, ionized states, and electron attached states. This is useful for theoretical and computational consistency and simplicity.

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