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Theoretical Investigation of the HOCO Radical in the Ground Electronic State

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Hydrocarboxyl radical, HOCO, plays an important role in the reaction between hydroxyl radical and carbon monoxid, $\text{HO}+\text{CO}\rightarrow\text{H}+\text{CO}_2$, which provides the most common pathway for atmospheric depletion of both OH and CO and is the principle source of heat in hydrocarbon flames. Our primary interest in HOCO arises from the new spectroscopic information¹, providing gas phase spectra of the *cis*-conformer for the first time. In the present work, the potential energy surface (PES) for HOCO for the ground electronic state ($X^2\Delta'$) was explored by means of the partially spin adapted coupled cluster RCCSD(T) method using the cc-pVQZ basis set. Ab initio calculations were designed such to cover the range of spectroscopic interest.

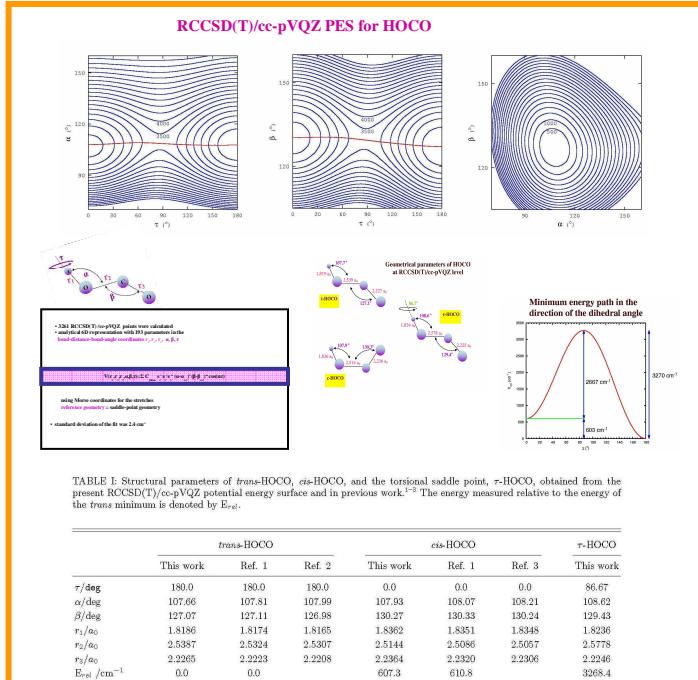
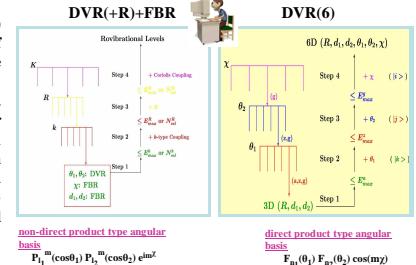


TABLE I: Structural parameters of *trans*-HOCO, *cis*-HOCO, and the torsional saddle point, τ -HOCO, obtained from the present RCCSD(T)/cc-pVQZ potential energy surface and in previous work.¹⁻³ The energy measured relative to the energy of the *trans* minimum is denoted by E_{rel} .

trans-HOCO			<i>cis</i> -HOCO			τ -HOCO		
This work	Ref. 1	Ref. 2	This work	Ref. 1	Ref. 3	This work		
τ/deg	180.0	180.0	180.0	0.0	0.0	0.0	86.67	
α/deg	107.66	107.81	107.99	107.93	108.07	108.21	108.62	
β/deg	127.07	127.11	126.98	130.33	130.24	129.43	129.43	
r_1/a_0	1.8186	1.8174	1.8165	1.8362	1.8351	1.8348	1.8236	
r_2/a_0	2.5387	2.5324	2.5307	2.5144	2.5086	2.5057	2.5578	
r_3/a_0	2.2265	2.2223	2.2208	2.2364	2.2320	2.2306	2.2246	
$E_{\text{rel}}/\text{cm}^{-1}$	0.0	0.0	607.3	610.8	610.8	3268.4		

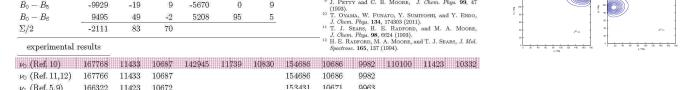
Vibrational and rovibrational ($J=0-4$) energy levels are obtained by means of computational strategies based on the discrete variable representation [DVR6] and the (functional-pointwise) coor. representations [DVR(R)+FBR] together with contraction schemes resulting from several diagonalization and truncation steps.^{2,3} Rotational constants computed for the ground vibrational state of *trans*-HOCO and *cis*-HOCO are in good agreement with the experimental values.



$$\begin{array}{l} \text{non-direct product type angular basis} \\ \mathbf{P}_1^m(\cos\theta_1) \mathbf{P}_2^m(\cos\theta_2) e^{im\chi} \\ \text{direct product type angular basis} \\ \mathbf{F}_{\mathbf{n}_1}(0_1) \mathbf{F}_{\mathbf{n}_2}(0_2) \cos(m\chi) \end{array}$$

TABLE III: Rotational constants (in MHz)

	trans-HOCO			<i>cis</i> -HOCO			trans-DOCO			<i>cis</i> -DOCO		
	A	B	C	A	B	C	A	B	C	A	B	C
theoretical results												
PB0	107760	115111	107711	142007	11827	10918	154022	10773	10005	109946	11503	10414
PForbenberry	107470	115381	107533	141807	11856	10942	154032	10774	10017	109476	11463	10378
PES	107766	114905	107299	141374	11784	10877	154044	10774	10017	109305	11348	10279
ave PBS	105392	113634	106344	141374	11683	10772	152386	10623	9934	10877	11202	10229
diff	834	102	85	107	12	105	1638	91	83	441	115	97
ω_{vib}	21.92	62	52	841	63	19.9	76	56	58	81	61	58
ω_{vib}	-14.8	17	-17	-1033	41	-87	82	78	230	71	64	64
ω_{vib}	-53	102	91	557	96	72	-766	20	-514	56	40	40
ω_{vib}	-2166	-7	-5	-2556	-1	10	-597	-4	4	-1456	6	10
ω_{vib}	1718	28	22	221	45	53	2286	14	-10	40	46	6
$\Sigma/2$	706	109	100	24	112	101	1035	115	97	240	132	99



P. BERNARDIN, *Mol. Phys.* **103**, 1441 (2005).
R. G. FORBENBERRY, R. HOUANG, J. S. FRANCK, T. D. COOPER, *J. Chem. Phys.* **117**, 1141 (2002).
C. DE FORBENBERRY, R. G. FORBENBERRY, T. D. COOPER, and T. J. LEE, *J. Chem. Phys.* **113**, 21403 (2000).
J. L. STREIBER AND C. B. MOORE, *J. Chem. Phys.* **113**, 10288 (2000).
J. L. STREIBER AND C. B. MOORE, *J. Mol. Spectrosc.* **143**, 149 (1990).
D. FOYER, M. E. JACOB, AND W. E. THOMPSON, *J. Chem. Phys.* **113**, 10289 (2000).
T. J. STAVIS, W. M. FETTY, AND P. M. JONES, *J. Chem. Phys.* **113**, 10290 (2000).
D. E. MULLEN AND M. E. JACOB, *J. Chem. Phys.* **114**, 10291 (2001).
J. L. STREIBER AND C. B. MOORE, *J. Chem. Phys.* **114**, 10292 (2001), and ref. therein.
T. OKADA, W. FETTY, Y. SHIMOMURA, AND Y. ENDO, *J. Chem. Phys.* **114**, 10293 (2001).
T. STAVIS, B. S. RAYMOND, AND M. A. MOORE, *J. Chem. Phys.* **114**, 10294 (2001), and T. J. STAVIS, *J. Mol. Spectrosc.* **165**, 127 (1994).

	trans-HOCO			<i>cis</i> -HOCO			trans-DOCO			<i>cis</i> -DOCO		
	This work	Ref. 2	Expt.	This work	Ref. 3	Expt.	This work	Ref. 4	Expt.	This work	Ref. 4	Expt.
ν_1	3648	3642	3639*	3401	3451	3310*	2691	2688	2647*	2558	2555	2456*
ν_2	1860	1865	1852*	1825	1823	1797*	1859	1845	1822*	1820	1814	1798*
ν_3	1237	1237	1237*	1230	1230	1204*	1234	1231	1221*	1221	1211	1145
ν_4	1051	1052	1048*	1059	1046	1040*	995	990	991	949	947	947
ν_5	507	501	501*	506	502	505*	538	538	537*	538	535	557*
ZPE	4556.6	4559.0	4557.0	4551.4	4551.4	4551.4	4552.7	4552.7	4552.7	4551.4	4551.4	4485.7

fundamental vibrational transitions and isotropic tensor (PT) of HOCO (in cm^{-1}). In addition to the full-dimensional (PVR6) vibrational energies (E_{vib}), the in-phase-bi-rotational energies (E_{vib}) calculated for the planar configuration and the effective torsional frequency (ω_{eff}) determined according to Eq (1) are also shown.

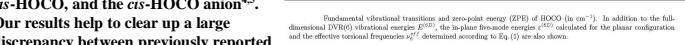


TABLE II: Fundamental vibrational transitions of HOCO and DOCO (in cm^{-1}).

	trans-HOCO			<i>cis</i> -HOCO			trans-DOCO			<i>cis</i> -DOCO		
	This work	Ref. 2	Expt.	This work	Ref. 3	Expt.	This work	Ref. 4	Expt.	This work	Ref. 4	Expt.
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ν_3	1237	1237	1237*	1230	1230	1204*	1234	1231	1221*	1221	1211	1145
ν_4	1054	1052.7	1048*	1050.0	1050.0	1025.2	1049	1045.4	1047	1046.9	1046.4	1047.4
ν_5	505	504	504	504	504	504	509	509	509	507	507	507.2
ZPE	4556.6	4559.0	4557.0	4551.4	4551.4	4551.4	4552.7	4552.7	4552.7	4551.4	4551.4	4485.7

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ν_5	505	504	504	504	504	504	509	509	509	507	507	507.2
ZPE	4556.6	4559.0	4557.0	4551.4	4551.4	4551.4	4552.7	4552.7	4552.7	4551.4	4551.4	4485.7

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ν_4												