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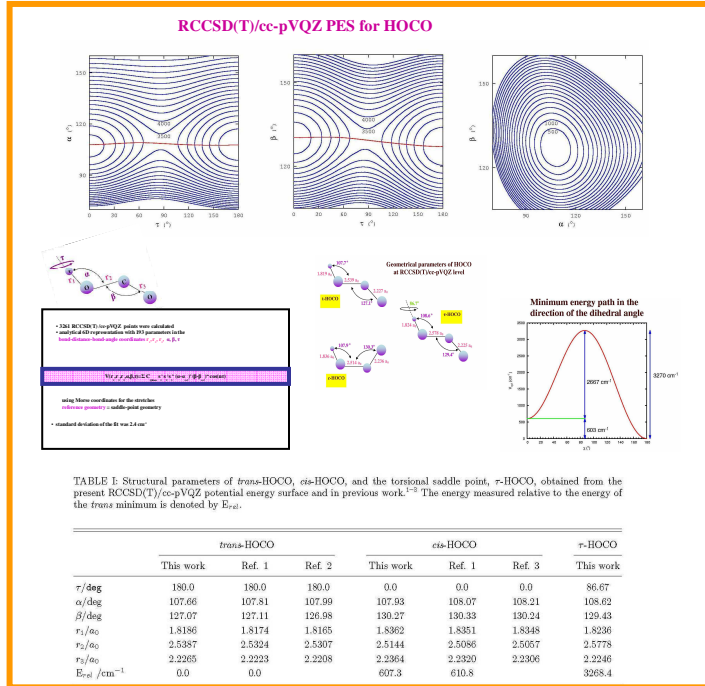
# Theoretical Investigation of the HOCO Radical in the Ground Electronic State

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Hydrocarboxyl radical, HOCO, plays an important role in the reaction between hydroxyl radical and carbon monoxide,  $\text{HO} + \text{CO} \rightarrow \text{H} + \text{CO}_2$ , 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 information<sup>1</sup>, 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 ( $X\ 2A'$ ) 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.



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) coordinates representations [DVR(+R)+FBR] together with contraction schemes resulting from several diagonalization and truncation steps.<sup>2,3</sup> Rotational constants computed for the ground vibrational state of *trans*-HOCO and *cis*-HOCO are in good agreement with the experimental values.

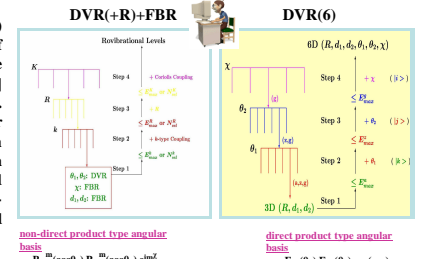
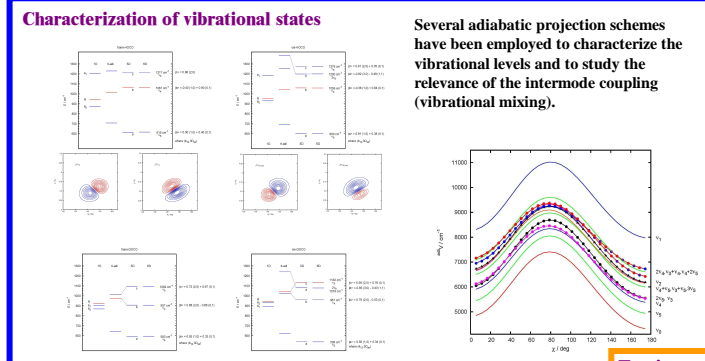
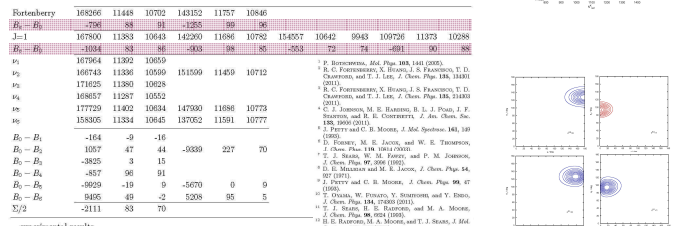


TABLE III. Rotational constants (in MHz)

Theoretical results	<i>trans</i> -HOCO			<i>cis</i> -HOCO			<i>trans</i> -DOCO			<i>cis</i> -DOCO		
	A	B	C	A	B	C	A	B	C	A	B	C
PBot	167700	11511	10771	142067	11827	10918	154922	10753	10055	109946	11503	10414
PRefineberry	167470	11538	10793	141897	11856	10942						
PES	166766	11495	10729	141357	11784	10877	154004	10714	10017	109476	11463	10376
ave PES	165932	11364	10634	141374	11653	10772	152368	10623	9934	109035	11348	10279
diff	834	102	85	-17	121	105	1638	91	83	441	115	197
ave $\mu_1$	21.10	16	23	1916	0	13	129	42	46	1766	-2	18
ave $\mu_2$	1262	62	62	941	63	63	1915	78	56	814	38	61
ave $\mu_3$	-1458	17	17	-1033	41	31	-897	82	78	230	71	64
ave $\mu_4$	-83	102	91	557	96	72	-766	20	20	-514	56	40
ave $\mu_5$	-2166	-7	5	-2556	-1	10	-597	-4	4	-1456	6	10
ave $\mu_6$	1718	28	2	221	45	53	2286	14	-10	40	46	6
$\Sigma/2$	706	109	100	24	112	121	1035	115	97	240	132	99



Numerically exact vibrational transitions are also presented for the quartic force fields developed recently for *trans*-HOCO, *cis*-HOCO, and the *cis*-HOCO anion<sup>4,5</sup>. Our results help to clear up a large discrepancy between previously reported vibrational perturbation theory (VPT) and vibrational configuration interaction (VCI) predictions for the torsional frequency.

