

# The Renner Effect in the $\tilde{X}^2A'$ and $\tilde{A}^2A''$ Electronic States of the HCO Radical

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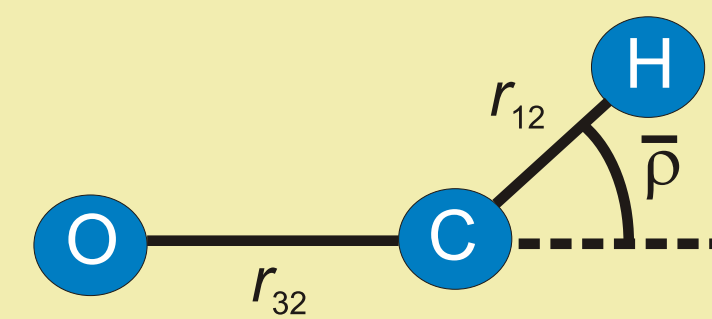
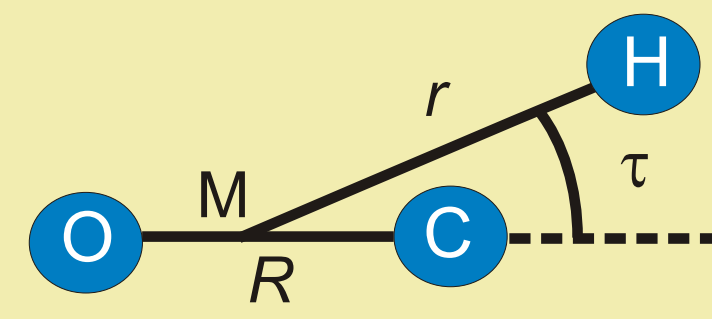
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Three-dimensional potential energy surfaces (PESs) and dipole moment surfaces (DMSs) for the  $\tilde{X}^2A'$  and  $\tilde{A}^2A''$  electronic states of the HCO radical have been calculated *ab initio* at the full-valence multi-reference single and double excitation configuration (MR-SDCI) + Davidson correction Q level of theory including core-valence correlations, based on the five-state (i.e., three  $A'$  and two  $A''$  states) averaged CASSCF orbitals, with basis sets of the Dunning aug-cc-pVQZ for H and aug-cc-pCVQZ for C and O.

The  $\tilde{X}^2A'$  and  $\tilde{A}^2A''$  states correlate with a  $^2\Pi$  state at H-C-O linear geometries so that they exhibit the Renner effect. We have applied the RENNER program [P. Jensen, M. Brumm, W. P. Kraemer and P. R. Bunker, J. Mol. Spectrosc. **171**, 31-57, (1995); M. Kolbuszewski, P.R. Bunker, P. Jensen and W. P. Kraemer, Mol. Phys. **88**, 105-124 (1996); G. Osmann, P. R. Bunker, P. Jensen and W. P. Kraemer, Chem. Phys. **225**, 33-54 (1997)] to calculate rovibronic energies and intensities for  $\tilde{X}^2A'$  and  $\tilde{A}^2A''$  HCO, using the *ab initio* PESs and DMSs described above.

The  $\tilde{X}^2A'$  state is repulsive for the Jacobi angle  $\tau$  in the interval 65-85° with a barrier to H+CO dissociation [see, for example, H. M. Keller, M. Stumpf, T. Schröder, C. Stock, F. Temps, R. Schinke, H.-J. Werner, C. Bauer, and P. Rosmus, J. Chem. Phys. **106**, 5359-5378 (1997), and references therein]. Since the RENNER program can calculate bound states only, the present work is concerned with low-lying bound rovibronic states, situated below the dissociation barrier, for  $\tilde{X}^2A'$  HCO.

The coordinates  $r, R, \tau, r_{12}, r_{32}$ , and  $\bar{\rho}$  used to describe the HCO radical. M is the center of mass of the CO moiety.



The *ab initio* energy points are fitted to the expansion

$$V_{\pm}(r_{12}, r_{32}, \bar{\rho}) = \sum_{\sigma} G_{\sigma}^{(\pm)} (y_1^{(\text{ref})})^\sigma (y_3^{(\text{ref})})^\sigma (1 - \cos \bar{\rho})^i$$

with

$$y_i^{(\text{ref})} = 1 - \exp[-a_i (r_{i2} - r_{i2}^{(\text{ref})})], i = 1 \text{ or } 3,$$

where  $i = 1$  is associated with the H-C bond, and  $i = 3$  with the CO bond.

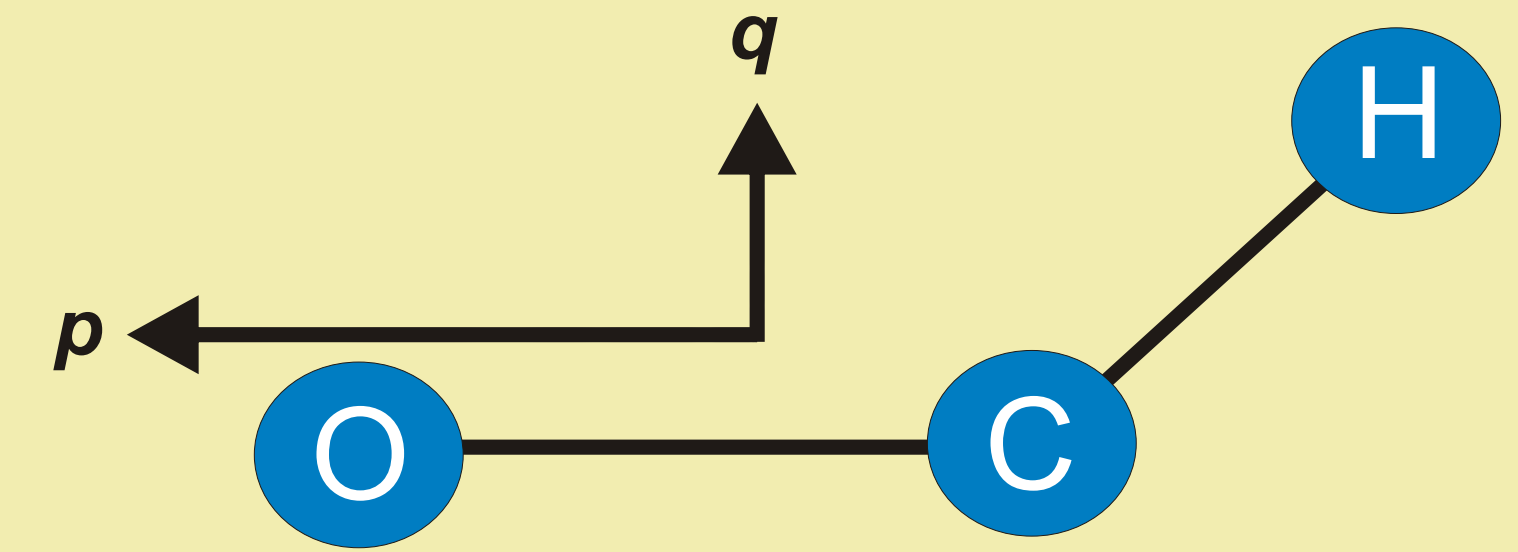
In the fitting, the *ab initio* were weighted such that points near the equilibrium structure of  $\tilde{X}^2A'$  are given weights of 1.0 while the weights are decreased with increasing electronic energy so that points around 25000 cm<sup>-1</sup> have weights of 0.01. Points with  $\tau \geq 65^\circ$  were given zero weight in the fitting. The input for the fitting consisted of 1315 points (658 points on the lower surface and 657 points on the upper surface). We could usefully vary 61 parameters and have achieved a standard deviation of 24.4 cm<sup>-1</sup>.

The potential energy surface parameters for the  $\tilde{X}^2A'$  and  $\tilde{A}^2A''$  electronic states of HCO

$G_{\sigma}^{(\pm)}$	$G_{\sigma}^{(\pm)}$	$G_{\sigma}^{(\pm)}$
$r_{12}^{(\text{ref})}/\text{Å}$	1.963366(14)	
$r_{32}^{(\text{ref})}/\text{Å}$	1.182339(15)	
$a_1/\text{Å}^{-1}$	2.0	
$a_3/\text{Å}^{-1}$	2.4	
$G_{000}/\text{cm}^{-1}$	2696.81574(11565)	
$G_{100}/\text{cm}^{-1}$	96648.206(7)	
$G_{200}/\text{cm}^{-1}$	64561.112(1)	
$G_{300}/\text{cm}^{-1}$	81713(6)	
$G_{400}/\text{cm}^{-1}$	-7092(16)	
$G_{500}/\text{cm}^{-1}$	11266(27)	
$G_{600}/\text{cm}^{-1}$	11052(180)	
$G_{700}/\text{cm}^{-1}$	-25002(27)	
$G_{010}/\text{cm}^{-1}$	-46097(17)	
$G_{020}/\text{cm}^{-1}$	273180(228)	
$G_{030}/\text{cm}^{-1}$	-845110(1370)	
$G_{040}/\text{cm}^{-1}$	181908(4396)	
$G_{050}/\text{cm}^{-1}$	-245897(7987)	
$G_{060}/\text{cm}^{-1}$	202949(16566)	
$G_{070}/\text{cm}^{-1}$	-948865(4484)	
$G_{080}/\text{cm}^{-1}$	194700(969)	
$G_{090}/\text{cm}^{-1}$	-626363(30)	
$G_{110}/\text{cm}^{-1}$	13236(34)	
$G_{120}/\text{cm}^{-1}$	150026(142)	
$G_{130}/\text{cm}^{-1}$	-263009(1)	
$G_{140}/\text{cm}^{-1}$	-203836(32)	
$G_{150}/\text{cm}^{-1}$	90865(5)	
$G_{160}/\text{cm}^{-1}$	89705(23)	
$G_{170}/\text{cm}^{-1}$	-10791(23)	
$G_{180}/\text{cm}^{-1}$	-4768(42)	
$G_{190}/\text{cm}^{-1}$	6607(23)	
$G_{210}/\text{cm}^{-1}$	12502(24)	
$G_{220}/\text{cm}^{-1}$	20451(689)	
$G_{230}/\text{cm}^{-1}$	-17213(442)	
$G_{240}/\text{cm}^{-1}$	-1305(7)	
$G_{250}/\text{cm}^{-1}$	-351004(70)	
$G_{260}/\text{cm}^{-1}$	-1186(55)	
$G_{270}/\text{cm}^{-1}$	10606(298)	
$G_{280}/\text{cm}^{-1}$	-3808(41)	
$G_{310}/\text{cm}^{-1}$	-46097(17)	
$G_{320}/\text{cm}^{-1}$	273180(228)	
$G_{330}/\text{cm}^{-1}$	-845110(1370)	
$G_{340}/\text{cm}^{-1}$	181908(4396)	
$G_{350}/\text{cm}^{-1}$	-245897(7987)	
$G_{360}/\text{cm}^{-1}$	202949(16566)	
$G_{370}/\text{cm}^{-1}$	-948865(4484)	
$G_{380}/\text{cm}^{-1}$	194700(969)	
$G_{390}/\text{cm}^{-1}$	-626363(30)	
$G_{410}/\text{cm}^{-1}$	13236(34)	
$G_{420}/\text{cm}^{-1}$	150026(142)	
$G_{430}/\text{cm}^{-1}$	-263009(1)	
$G_{440}/\text{cm}^{-1}$	-203836(32)	
$G_{450}/\text{cm}^{-1}$	90865(5)	
$G_{460}/\text{cm}^{-1}$	89705(23)	
$G_{470}/\text{cm}^{-1}$	-10791(23)	
$G_{480}/\text{cm}^{-1}$	-4768(42)	
$G_{490}/\text{cm}^{-1}$	6607(23)	
$G_{510}/\text{cm}^{-1}$	12502(24)	
$G_{520}/\text{cm}^{-1}$	20451(689)	
$G_{530}/\text{cm}^{-1}$	-17213(442)	
$G_{540}/\text{cm}^{-1}$	-1305(7)	
$G_{550}/\text{cm}^{-1}$	-351004(70)	
$G_{560}/\text{cm}^{-1}$	-1186(55)	
$G_{570}/\text{cm}^{-1}$	10606(298)	
$G_{580}/\text{cm}^{-1}$	-3808(41)	

Units are cm<sup>-1</sup> unless otherwise indicated.  $G_{000} + G_{100} + G_{200}$  is  $G_{000}^{(\pm)}$ . The subscript  $i$  refers to the H-C bond, whereas the subscript  $j$  refers to the C-O bond. Parameters for which no standard error is given, were held fixed in the least squares fit. Quantities in parentheses are standard errors in units of the last digit given.

The axis system  $xpq$  used to describe the dipole moment components and the transition moment for the  $\tilde{X}^2A'$  and  $\tilde{A}^2A''$  electronic states of the HCO radical. The origin is at the nuclear center of mass, the  $p$  axis is parallel to the CO bond, and the  $x$  axis is chosen such that  $xpq$  is right-handed.



Dipole moment parameters for the  $\tilde{X}^2A'$  and  $\tilde{A}^2A''$  electronic states of HCO

Quantities in parentheses are standard errors in units of the last digit given, and  $\sigma$  is the standard deviation of the fitting.

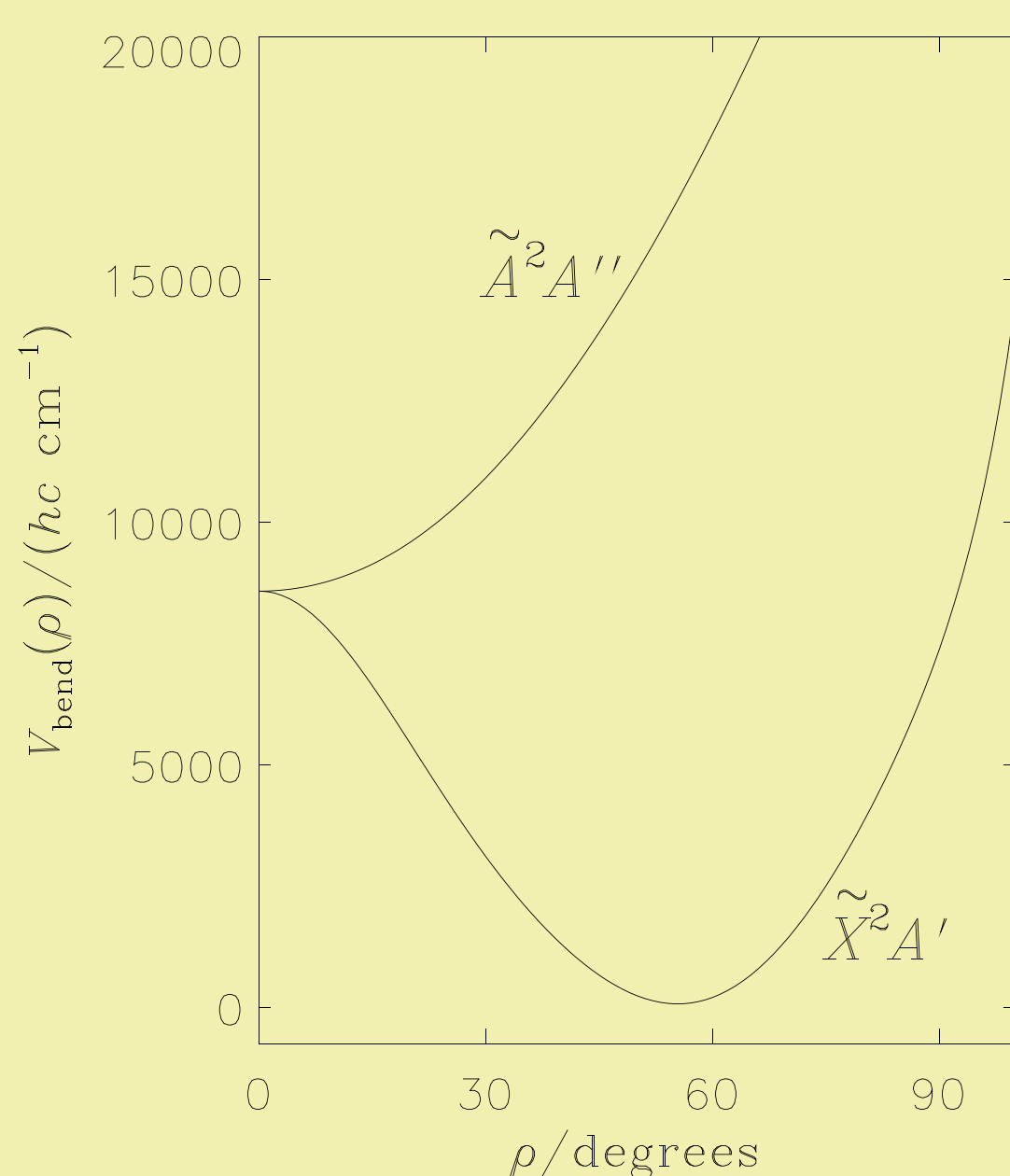
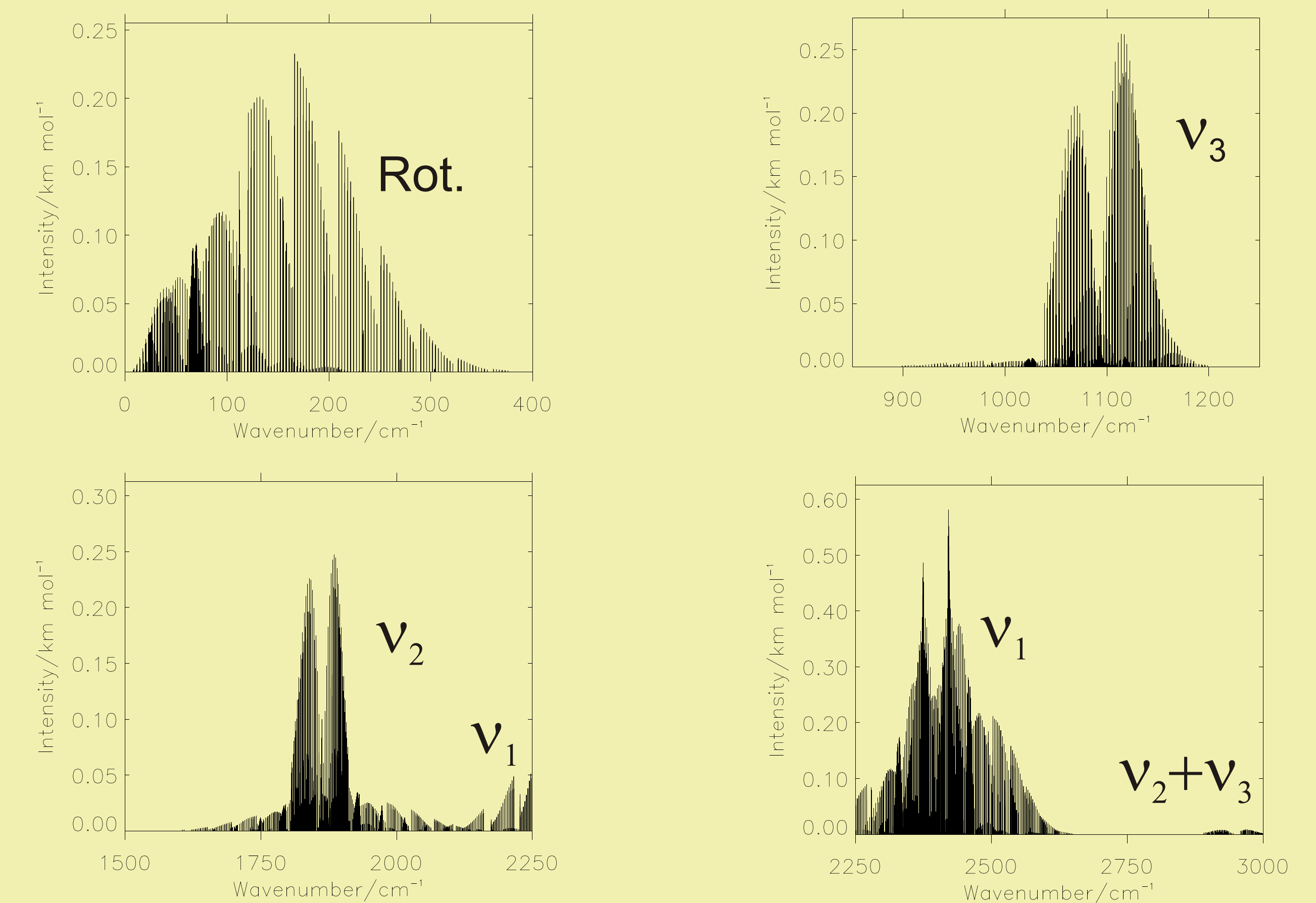
$\tilde{X}^2A'$ ( $\sigma = \dots$ )	$\tilde{X}^2A''$ ( $\sigma = \dots$ )	$\tilde{A}^2A''$ ( $\sigma = \dots$ )
$\mu_{\rho}^{(\sigma)}/\text{D}$	2.0313(88)	2.0205(10)
$\mu_{\tau}^{(\sigma)}/\text{D}$	-5.02(18)	-1.267(21)
$\mu_{\bar{\rho}}^{(\sigma)}/\text{D}$	18.3(10)	-0.56(12)
$\mu_{\tau}^{(\sigma)}/\text{D}$	-36.8(25)	1.2(125)
$\mu_{\bar{\rho}}^{(\sigma)}/\text{D}$	32.8(27)	-1.32(21)
$\mu_{\tau}^{(\sigma)}/\text{D}$	-10.9(10)	0.385(61)
$\mu_{\bar{\rho}}^{(\sigma)}/\text{D}$	-0.824(71)	1.100(11)
$\mu_{\tau}^{(\sigma)}/\text{D}$	-0.21(13)	-1.057(47)
$\mu_{\bar{\rho}}^{(\sigma)}/\text{D}$	-5.09(32)	0.680(69)
$\mu_{\tau}^{(\sigma)}/\text{D}$	3.87(55)	-0.81(16)
$\mu_{\bar{\rho}}^{(\sigma)}/\text{D}$	3.36(59)	0.882(26)
$\mu_{\tau}^{(\sigma)}/\text{D}$	3.21(17)	2.506(21)
$\mu_{\bar{\rho}}^{(\sigma)}/\text{D}$	-0.76(31)	-1.108(87)
$\mu_{\tau}^{(\sigma)}/\text{D}$	-3.3(17)	-3.68(39)
$\mu_{\bar{\rho}}^{(\sigma)}/\text{D}$	11.9(19)	0.000000
$\mu_{\tau}^{(\sigma)}/\text{D}$	-8.3(26)	0.0028
$\mu_{\bar{\rho}}^{(\sigma)}/\text{D}$	0.03	0.0028
$\mu_{\tau}^{(\sigma)}/\text{D}$	2.341(23)	0.8301(23)
$\mu_{\bar{\rho}}^{(\sigma)}/\text{D}$	-7.99(33)	0.470(31)
$\mu_{\tau}^{(\sigma)}/\text{D}$	23.7(15)	-0.74(13)
$\mu_{\bar{\rho}}^{(\sigma)}/\text{D}$	-35.8(32)	-0.50(24)
$\mu_{\tau}^{(\sigma)}/\text{D}$	25.9(31)	1.02(18)
$\mu_{\bar{\rho}}^{(\sigma)}/\text{D}$	-7.1(11)	-0.305(50)
$\mu_{\tau}^{(\sigma)}/\text{D}$	-2.134(85)	1.275(18)
$\mu_{\bar{\rho}}^{(\sigma)}/\text{D}$	-2.49(36)	-0.929(96)
$\mu_{\tau}^{(\sigma)}/\text{D}$	1.51(15)	0.805(31)
$\mu_{\bar{\rho}}^{(\sigma)}/\text{D}$	-7.8(37)	1.24(62)
$\mu_{\tau}^{(\sigma)}/\text{D}$	-1.02(30)	-1.579(92)
$\mu_{\bar{\rho}}^{(\sigma)}/\text{D}$	9.0(53)	-4.1(10)
$\mu_{\tau}^{(\sigma)}/\text{D}$	1.11(13)	0.168(39)
$\mu_{\bar{\rho}}^{(\sigma)}/\text{D}$	1.684(47)	0.32(11)
$\mu_{\tau}^{(\sigma)}/\text{D}$	10.4(13)	3.30(48)
$\mu_{\bar{\rho}}^{(\sigma)}/\text{D}$	0.022	0.0016

where  $i = 1$  is associated with the H-C bond, and  $i = 3$  with the CO bond.

The transition moment between the  $\tilde{X}^2A'$  and  $\tilde{A}^2A''$  electronic states is fitted to

$$\mu_{\rho}^{(\sigma)}(r_{12}, r_{32}, \bar{\rho}) = \sin \bar{\rho} \sum_{\sigma} x_{j0}^{(\sigma)} (\Delta r_{12}^{(\text{ref})})^\sigma \times (\Delta r_{32}^{(\text{ref})})^\sigma (1 - \cos \bar{\rho})^i$$

We have used RENNER to simulate the absorption spectra of  $\tilde{X}^2A'$  HCO in the wavenumber region up to 3000 cm<sup>-1</sup>. The simulations are done at the absolute temperature  $T = 273$  K and involves states with  $J \leq 35/2$ . The basis set is identical to that used for the energy calculations.



The pure bending potentials  $V_{\pm}(r_{12}^{(\text{ref})}, r_{32}^{(\text{ref})}, \bar{\rho})$  plotted for the  $\tilde{X}^2A'$  and  $\tilde{A}^2A''$  electronic states of HCO.

Fundamental term values (in cm<sup>-1</sup>) for the  $\tilde{X}^2A'$  electronic state of HCO

		Experiment						Theory					
		M69	D69	L81	H86	M86	S90	T95	B86	C88	W95	SA98	PW
HCO	$v_1$	2483	2440	2435	2448	2448	2642	2446	2443	2443	2399		
	$v_2$	1863	1868	1868	1885	1885	1975	1844	1851	1863			
	$v_3$	1087	1081	1087	1104	1104	1126	1072	1072	1091			
DCO	$v_1$	1926	1937	1910			1930	2049	1894	1904			
	$v_2$	1803	1800	1795			1809	1883	1789	1766			
	$v_3$	850	852	847			865	882	835	856			
D <sup>13</sup> CO	$v_1$		1910						1867	1867			
	$v_2$		1780						1770	1753			
	$v_3$			845					828	848			
H <sup>13</sup> CO	$v_1$				2437				2437	2392			
	$v_2$		1821		1829				1811	1823			
	$v_3$		1084		1074				1065	1084			
HC <sup>18</sup> O	$v_1$				2441				2442	2397			
	$v_2$				1824				1806	1816			
	$v_3$				1076				1068	1087			

M69 IR and UV spectra in CO and argon matrices; D. E. Miligan and M. E. Jacox, J. Chem. Phys. **41**, 3032 (1964); D. E. Miligan and M. E. Jacox, J. Chem. Phys. **51**, 277 (1969)  
D69 Fit of matrix data (G. E. Ewing, W. Thompson, and G. C. Pimentel, J. Chem. Phys. **32**, 927 (1960) including anharmonicity from the CH stretching [R. N. Dixon, J. Mol. Spectrosc. **30**, 248 (1959)]  
L81 Laser magnetic resonance data [R. S. Loew and A. R. W. McKellar, J. Chem. Phys. **74**, 2688 (1981); Absorption spectroscopy for  $v_1$  [J. M. Brown and D. A. Ramsay, Can. J. Phys. **83**, 2232 (1975)]  
H86 E. Hirota, J. Mol. Struct. **146**, 237 (1986)  
M86 Photoelectron spectroscopy in gas phase; K. K. Murray, T. M. Miller, D. G. Leopold, and W. C. Lineberger, J. Chem. Phys. **84**, 2820 (1986)  
S90 Laser induced fluorescence in gas phase; A. D. Sappay and D. R. Crosby, J. Chem. Phys. **93**, 7601 (1990)  
T95 Dispersed fluorescence in jet-cooled HCO; J. D. Tobiasson, J. R. Dunkop, and E. A. Rohlfing, J. Chem. Phys. **103**, 1448 (1995)  
B86 SDCHQSDP *ab initio*; J. M. Bowman, J. S. Bhattarai, and L. B. Harding, J. Chem. Phys. **85**, 911 (1986)  
C88 SDCHQSDP *ab initio*; D. A. Case, W. D. Allen, R. B. Remington, Y. Yamaguchi, and H. F. Schaefer III, Chem. Phys. **123**, 187 (1989)  
W95 ICHQVQZ3P-2T *ab initio*; H. J. Werner, C. Bauer, P. Rosmus, H. M. Keller, M. Stumpf, and R. Schinke, J. Chem. Phys. **102**, 3593 (1995)  
SA98 CASPT2/VZ2P-*ab initio*; L. Serrano-Andres, N. Forsberg, P.-Å. Malmqvist, J. Chem. Phys. **108**, 7202 (1998)  
PW Present work

We have used RENNER to calculate the fundamental vibrational energies ( $v_1$ : H-C stretch,  $v_2$ : bending mode, and  $v_3$ : C-O stretch) for various isotopologues of  $\tilde{X}^2A'$  HCO, and we have compared the results with the available experimental data and the results of other theoretical calculations.

We see that the  $v_2$  values are in rather good agreement with experiment whilst the agreement is less satisfactory for  $v_1$  and  $v_3$ . Presumably, the reason is that our set of *ab initio* points does not, as yet, involve sufficiently large displacements of  $r_{12}$  and  $r_{32}$ . Work with calculating more *ab initio* points is in progress.