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The molecular structure and analytical potential energy function of HCO (X^2A')*

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In this paper the equilibrium structure of HCO has been optimized by using density functional theory (DFT)/ B3P86 method and CC-PVTZ basis. It has a bent (C_s, X^2A') ground state structure with an angle of 124.4095°. The vibronic frequencies and force constants have also been calculated. Based on the principles of atomic and molecular reaction statics, the possible electronic states and reasonable dissociation limits for the ground state of HCO molecule have been determined. The analytic potential energy function of HCO (X^2A') molecule has been derived by using the many-body expansion theory. The contour lines are constructed, which show the static properties of HCO (X^2A'), such as the equilibrium structure, the lowest energies, etc. The potential energy surface of HCO (X^2A') is reasonable and very satisfactory.

Keywords: HCO (formyl radical), analytical potential energy function, many-body expansion theory

PACC: 3110, 3120D, 3130, 3520D

1. Introduction

The molecular potential energy function is the eigen energy of electron for a given electronic state in the fixed-nuclei and Born–Oppenheimer approximation, it is the complete description of molecular electronic energy and the potential function of nuclear motion, and it is also the base of studying the atomic and molecular collision and molecular reaction dynamics.[1−3] HCO is an unstable molecule, and it can easily react with other molecules.[4,5] Moreover, it is the important active intermediate in the atmospheric chemistry, organismal oxidation and burnable process, then it requires to further study the reactive mechanism of HCO molecule with other molecules in the atmosphere. The relevant study has potential application value and important significance to protect environment. Up to now, the potential function of HCO molecule in many-body expansion form has not been reported in the literature.

In this work, we report many-body expansion potential energy function of HCO based on *ab initio* calculation and many-body expansion theory.[6] This method has been applied for some long periodic molecules,[7−9] but there are fewer studies for the short periodic molecules.[10] All calculations were carried out with DFT (B3P86)/ CC-PVTZ method[11] and performed by Gaussian 03 program.

2. Theoretical details

2.1. Electronic states and dissociation limits

For calculation and description of the full space potential function for HCO, we must determine the possible electronic states and its reasonable dissociation limits. Based on atomic and molecular reaction statics (AMRS)[12] and quantum mechanical calculation, the ground electronic states of HCO have been obtained.

Firstly, we derive the electronic states by using the separated atomic method.[12] The ground elec-

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tronic states for H, C and O are ^2S_g, ^3P_g and ^3P_g, respectively, they are SU (n) group,[13] while HCO molecule belongs to C_s group. According to the fact that the irreducible representation of the SU (n) group can be resolved into those of the C_s group to obtain the possible electronic states, then H (^2S_g), C (^3P_g) and O (^3P_g) are resolved into the direct sum of irreducible representations of C_s group as follows:

$$^2S_g \rightarrow {}^2A', \quad ^3P_g \rightarrow {}^3A' \oplus 2\,{}^3A'',$$

$$^3P_g \rightarrow {}^3A' \oplus 2\,{}^3A''.$$

When HC is in the ground state $X^2\Pi$, it can be decomposed into the direct sum of irreducible representations of C_s ($\sigma_h \rightarrow \sigma$) group for $2\ ^2A''$, their direct product and reduction of the ground state of HC with O (^3P_g) are

$$2\,{}^2A'' \oplus ({}^3A' \oplus 2\,{}^3A'') \rightarrow 2\,{}^{2,4}A'' \oplus 4\,{}^{2,4}A'. \quad (1)$$

We find that Eq.(1) includes $^2A'$, there are twelve states $2\ ^{2,4}A''$ and $4\ ^{2,4}A'$ in the combination HCO (C_s) molecule by the ground state HC ($X^2\Pi$) with O (^3P_g), it can be described as follows:

$$\begin{array}{ccccc} \mathrm{O} & + & \mathrm{HC} & \rightarrow & \mathrm{HCO}, \\ ^3P_g & & ^2\Pi & & 2\,{}^{2,4}A'' \oplus 4\,{}^{2,4}A'. \end{array}$$

When HO is in the ground state $X^2\Pi$ and C atom in the ground state ^3P_g, the condition is the same as the above, it also contains $^2A'$, so

$$\begin{array}{ccccc} 2\,{}^2A'' \oplus ({}^3A' \oplus 2\,{}^3A'') & & & \rightarrow & 2\,{}^{2,4}A'' \oplus 4\,{}^{2,4}A', \\ \mathrm{C} & + & \mathrm{HO} & \rightarrow & \mathrm{HCO}, \\ ^3P_g & & ^2\Pi & & 2\,{}^{2,4}A'' \oplus 4\,{}^{2,4}A'. \end{array} \quad (2)$$

If CO in the ground state $\mathrm{X}^1\Sigma^+$ and H atom in ^2S_g, the result is that:

$$\begin{array}{ccccc} A' & \oplus & {}^2A' & \rightarrow & {}^2A', \\ \mathrm{H} & + & \mathrm{CO} & \rightarrow & \mathrm{HCO}, \\ {}^2A' & & {}^1\Sigma^+ & & {}^2A'. \end{array} \quad (3)$$

Similarly, when H, C and O atoms all are in the ground states ^2S_g, ^3P_g and ^3P_g, their direct product and reduction are as follows:

$$\begin{aligned} &{}^2A' \oplus ({}^3A' \oplus 2\,{}^3A'') \oplus ({}^3A' \oplus 2\,{}^3A'') \\ &\rightarrow 5\,{}^{2,4}A' \oplus 4\,{}^{2,4}A'' \oplus 5\,{}^{2,4,6}A' \oplus 4\,{}^{2,4,6}A''. \end{aligned} \quad (4)$$

Equation (4) also contains $^2A'$. So it can be described as

$$\begin{array}{ccc} \mathrm{H} + \mathrm{C} + \mathrm{O} & \rightarrow & \mathrm{HCO}, \\ ^2S_g\ {}^3P_g\ {}^3P_g & & 5\,{}^{2,4}A' \oplus 4\,{}^{2,4}A'' \oplus 5\,{}^{2,4,6}A' \oplus 4\,{}^{2,4,6}A''. \end{array}$$

Therefore, according to the principle of microscopic reversibility,[12] the possible dissociation processes for HCO molecule can be expressed as:

$$\mathrm{HCO}(X^2A') \rightarrow \begin{cases} \mathrm{O}(^3P_g) + \mathrm{HC}(X^2\Pi), \\ \mathrm{C}(^3P_g) + \mathrm{HO}(X^2\Pi), \\ \mathrm{H}(^2S_g) + \mathrm{CO}(X^1\Sigma^+), \\ \mathrm{H}(^2S_g) + \mathrm{C}(^3P_g) + \mathrm{O}(^3P_g). \end{cases} \quad (5)$$

2.2. The equilibrium geometry and vibronic frequencies of HCO (X^2A') molecule

The doublet and quartet states of the ground state HCO molecule with angular structure have been optimized with DFT/B3P86, CCSD, QCISD methods and 6-311++G**, CC-PVTZ bases, we find that the doublet state energy of the ground state HCO molecule with angular structure is the lowest with B3P86/ CC-PVTZ method, and the bond length, bond angle all close to the experimental values. It belongs to C_s group. The equilibrium geometry, force constants and vibronic frequencies of the ground state HCO molecule have been calculated too, it takes on $^2A'$ electronic state. The results show that $\angle\mathrm{HCO} = 124.4095°$, $R_{\mathrm{H-C}} = 0.1171\,\mathrm{nm}$, $R_{\mathrm{C-O}} = 0.1123\,\mathrm{nm}$, $E = -114.1564$a.u., and vibronic frequencies as follows: symmetrical stretching vibronic frequency is $1107.1\mathrm{cm}^{-1}$, bent vibronic frequency is $1955.4\,\mathrm{cm}^{-1}$ and dissymmetry stretching vibronic frequency is $2673.4\,\mathrm{cm}^{-1}$.

To calculate the dissociation energy of HCO (X^2A') corresponding to the dissociation limit H (^2S_g) + C(^3P_g) + O (^3P_g) at the B3P86/ CC-PVTZ level, firstly, we calculate the energy for HCO (X^2A'), which is -114.1564a.u., then for C (^3P_g), H(^2S_g) and O (^3P_g), which are -37.8846a.u., -0.5185a.u. and -75.1189a.u., respectively, so the dissociation energy of HCO (X^2A') is: $D_e = E(\mathrm{C}) + E(\mathrm{H}) + E(\mathrm{O}) - E(\mathrm{HCO}) = 17.27\,\mathrm{eV}$. The results are all listed in Table 1, the experimental values are in the bracket.[4]

Table 1. The equilibrium structural parameters and force constants for HCO (X^2A').

Bond length/nm	$R = R_{\mathrm{H-C}} = 0.1171$ (0.1109) $r = R_{\mathrm{C-O}} = 0.1123$ (0.1152)
Bond angle/(°)	$\theta = \angle\mathrm{HCO} = 124.4095$ (126.6)
Dissociation energy [a]/eV	17.27
Force constants b	$f_{11} = 1.01293$ $f_{22} = 0.25433$ $f_{12} = 0.04732$ $f_{1\theta} = 0.03373$ $f_{2\theta} = 0.01877$ $f_{\theta\theta} = 0.16680$

[a] Relative to the dissociation limit H (^2S_g)+ C (^3P_g) + O (^3P_g).
[b] The units are in atomic units.

2.3. Many-body expansion analytical potential energy function of HCO (X^2A') molecule

The analytical potential energy function[14,15] and potential energy surface of triatomic molecules are the bases of studying the molecular reaction dynamics, and the latter is a hypersurface in the three-dimensional space.[6] If we choose the energy of ground state to be zero that satisfies with Eq.(5), the many-body expansion analytical potential energy function[6] of the ground state HCO (X^2A') molecule is:

$$V = V^{(2)}_{\mathrm{HC}}(R_1) + V^{(2)}_{\mathrm{CO}}(R_2) + V^{(2)}_{\mathrm{HO}}(R_3) + V^{(3)}_{\mathrm{HCO}}(R_1, R_2, R_3). \quad (6)$$

In Eq.(6), $R_1 = R_{\mathrm{H-C}}$, $R_2 = R_{\mathrm{C-O}}$, $R_3 = R_{\mathrm{H-O}}$, $V^{(2)}_{\mathrm{HC}}(R_1)$, $V^{(2)}_{\mathrm{CO}}(R_2)$, $V^{(2)}_{\mathrm{HO}}(R_3)$ are the two-body terms represented by the potential functions of HC($X^2\Pi$), CO($X^1\Sigma^+$) and HO($X^2\Pi$) respectively, and $V^{(3)}_{\mathrm{HCO}}(R_1, R_2, R_3)$ is the three-body term, which will be zero if any one of the atoms is removed to infinity. We will impose Murrell–Sorbie (M–S) potential function on the two-body terms:[6]

$$V = -D_{\mathrm{e}}(1 + a_1\rho + a_2\rho^2 + a_3\rho^3)\exp(-a_1\rho).$$

Where $\rho = R - R_{\mathrm{e}}, R$ and R_{e} are the diatomic distance and its equilibrium value respectively, D_{e} is dissociation energy and a_1, a_2, a_3 are the two-body terms fitting parameters of M–S potential energy function. The potential energy values of HC($X^2\Pi$), CO($X^1\Sigma^+$) and HO($X^2\Pi$) have been scanned by the same *ab initio* method. Force constants of the M–S function are calculated by the following formulae:

$$f_2 = D_{\mathrm{e}}(a_1^2 - 2a_2),$$

$$f_3 = -6D_{\mathrm{e}}\left(a_3 - a_1a_2 + \frac{1}{3}a_1^3\right),$$

$$f_4 = D_{\mathrm{e}}(3a_1^4 - 12a_1^2a_2 + 24a_1a_3).$$

The two-body terms parameters of potential energy function, force constants of HC, CO and HO molecules and the experimental values[6] are all listed in Table 2. Here, we mainly derive the three-body terms.

Table 2. The M–S potential energy functional parameters, force constants for HC, CO and HO molecules.

Molecule	D_{e}/eV	R_{e}/nm	a_1/nm^{-1}	a_2/nm^{-2}	a_3/nm^{-3}	f_2/(aJ · nm^{-2})	f_3/(aJ · nm^{-3})	f_4/(aJ · nm^{-4})
HC($X^2\Pi$)	3.839	0.1100	38.059	303.03	1765.7	517.453	−31726.76	1621559.6
Expt.	3.640	0.1120	38.319	349.90	2260.6	447.606	−26585.68	1387182.9
CO($X^1\Sigma^+$)	11.528	0.1100	38.491	221.65	1895.3	1915.044	−136926.53	8106925.7
Expt.	11.226	0.1128	39.038	232.53	1902.9	1901.893	−136390.40	8078537.3
HO($X^2\Pi$)	4.938	0.1000	44.861	479.64	3784.1	832.135	−58598.80	3667097.8
Expt.	4.621	0.0970	45.129	490.55	3809.9	780.420	−54605.13	3387317.5

To obtain the many-body expansion potential energy function, it requires to choose appropriate reference coordinates. Where we choose $C_{2\mathrm{v}}$ symmetry ($R_1^0 = R_{\mathrm{H-C}} = 0.1171\,\mathrm{nm}$, $R_2^0 = R_{\mathrm{C-O}} = 0.1123\,\mathrm{nm}$, $R_3^0 = R_{\mathrm{H-O}} = 0.2030\,\mathrm{nm}$) as the reference structure, then the symmetrical internal coordinates S_1, S_2 and S_3 are given by the following transformation[6]

$$\begin{pmatrix} S_1 \\ S_2 \\ S_3 \end{pmatrix} = \begin{pmatrix} 1/\sqrt{2} & 1/\sqrt{2} & 0 \\ 1/\sqrt{2} & 1/\sqrt{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \rho_1 \\ \rho_2 \\ \rho_3 \end{pmatrix}. \quad (7)$$

Where the internal coordinates ρ_i are given by $\rho_i = R_i - R_i^0 \quad (i = 1, 2, 3)$.

The three-body term of Eq.(6) can be written in symmetric internal coordinates as

$$V_{\mathrm{HCO}}^{(3)}(R_1, R_2, R_3) = PT. \tag{8}$$

Here P is a polynomial

$$\begin{aligned} P = \; & C_0 + C_1 S_1 + C_2 S_3 + C_3 S_2^2 + C_4 S_3^2 \\ & + C_5 S_1 S_3 + C_6 S_3^4 + C_7 S_1^2 + C_8 S_1 (S_2^2 + S_3^2) \\ & + C_9 S_2 S_3^2, \end{aligned} \tag{9}$$

and T is a range function

$$\begin{aligned} T = \; & [1 - \tanh(\gamma_1 S_1/2)][1 - \tanh(\gamma_2 S_2/2)] \\ & \times [1 - \tanh(\gamma_3 S_3/2)]. \end{aligned} \tag{10}$$

To gain $V_{\mathrm{HCO}}^{(3)}(R_1, R_2, R_3)$, we need to determine ten linear parameters C_1–C_{10} in polynomial P and three non-linear ones $\gamma_1, \gamma_2, \gamma_3$ in range function T. The non-linear ones can be determined by optimizing the potential energy surface and the linear ones by using the equilibrium structure, dissociation energy and force constants (in Table 1). The parameters are listed in Table 3. Finally, we can plot the contours of the potential according to analytical potential energy function Eq.(6), as shown in Figs.1–4.

Table 3. The three body term parameters of analytical potential energy function for HCO.

C_0	C_1	C_2	C_3	C_4	C_5	
1.611726	−12.938791	−16.765451	3.041088	−1.447831	−4.221487	
C_6	C_7	C_8	C_9	γ_1	γ_2	γ_3
−1.730625	25.897598	27.596401	−8.565447	1.85	1.85	1.85

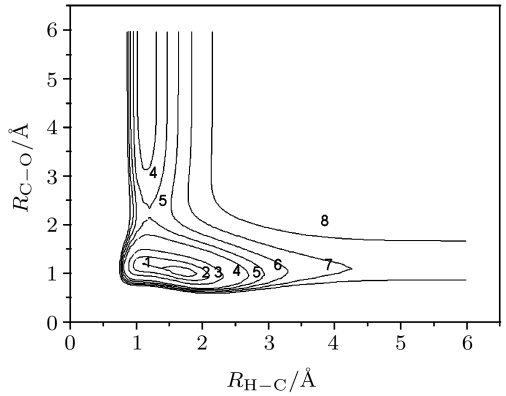


Fig.1. H–C and C–O bonds stretching contours for HCO (X^2A'). E(eV): 1. −17.2, 2. −16.0, 3. −14.0, 4. −10.0, 5. −8.0, 6. −6.0, 7. −4.0, 8. −2.0.

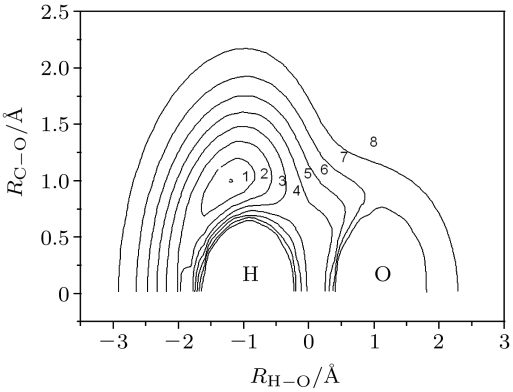


Fig.2. Contour lines of HCO (X^2A') for C atom moving around the H–O bond. E(eV): 1. −17.2, 2. −16.0, 3. −14.0, 4. −12.0, 5. −10.0, 6. −8.0, 7. −6.0, 8. −4.0.

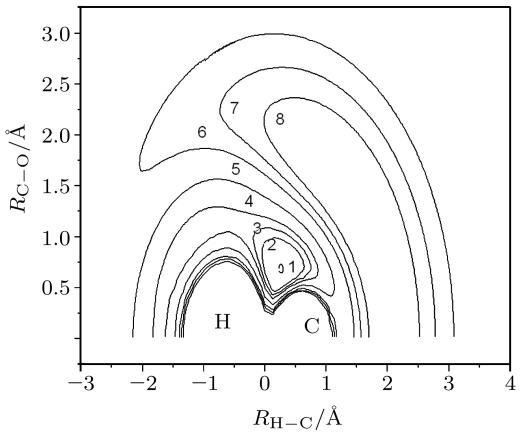


Fig.3. Contour lines of HCO (X^2A') for O atom moving around the H–C bond. E(eV): 1. −24.5, 2. −2.0, 3. −18.0, 4. −16.0, 5. −12.0, 6. −8.0, 7. −6.0, 8. −4.0.

3. Results and discussion

Figures 1–4 are the contours of potential for the HCO (X^2A') molecule. They clearly reproduce the character of the ground state HCO (X^2A') molecule in equilibrium structure. Figure 1 shows the H–C and C–O bonds stretching contour for a fixed angle $\angle$HCO = 124.4095°, which represents the stretched and vibronic condition of H–C and C–O bonds. From this figure, we can see that there is a potential well (−17.2 eV) at $R_{\mathrm{H-C}}$ = 0.1171 nm and $R_{\mathrm{C-O}}$ =

0.1123 nm, which accords with the dissociation energy (−17.265 eV) of equilibrium structure. Simultaneously, there is a saddle point at $R_{H-C} = 0.1171$ nm and $R_{C-O} = 0.2030$ nm. These illuminate that if C atom attacks H–O bond from H sideways, it will more easily make a steady HCO molecule than from O. Moreover, there does not exist an evident potential barrier during the reaction. Consequently, this could be a non-threshold energy reaction, and it can easily occur.

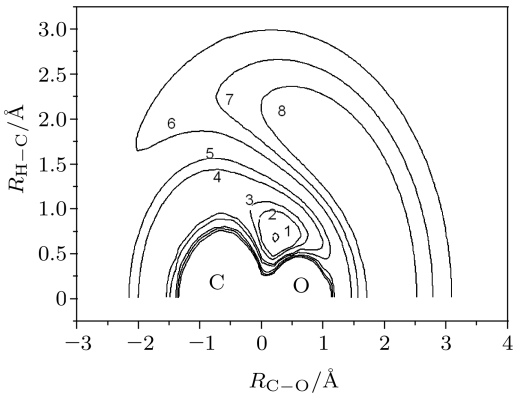


Fig.4. Contour lines of HCO (X^2A') for H atom moving around the C–O bond. E(eV): 1. −24.5, 2. −20.0, 3. −18.0, 4. −14.0, 5. −12.0, 6. −8.0, 7. −6.0, 8. −4.0.

Figure 2 shows the contours for C atom moving around the fixed H–O bond, the lowest energy is at point 1 (−17.2 eV), the contours reproduce the C_s symmetrical structure of HCO (X^2A'). HCO molecule could form easily if C atom attacks HO from H atom side, the angle is about 124.4095°, this also accords with the optimum structure. It is in agreement with the result of Fig 1. Figures 3 and 4 show the contours for O atom moving around the fixed H–C bond and H around C–O bond respectively. From the two figures, we can see that if O atom or H atom attacks H–C bond or C–O bond, it will be more difficult than attacking H–O bond from C atom, for it needs more energy to carry through the reaction.

4. Conclusions

The equilibrium geometry, force constants and vibronic frequencies of HCO (X^2A') have been calculated with B3P86/CC-PVTZ method. Afterward, we further scan the whole potential curves for the ground state of HC, CO and HO molecules by using the same method, and finally employ a least square method to fit the potential in M–S function, which obtains the corresponding M–S potential parameters and force constants. Based on the principles of atomic and molecular reaction statics, the dissociation limits of HCO (X^2A') are determined. For the first time, we report the potential function of HCO in many-body expansion form. The contours of the potential clearly reproduce the character of the ground state HCO molecule in equilibrium structure, at the same time, they show that C + HO → HCO is a non-threshold energy reaction, and it occurs more easily than other dissociation channels. The above results are helpful for the dynamic and spectrum studies of HCO.

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