Rotational analysis and line intensities of the HCO $\tilde{B}^2A'$–$\tilde{X}^2A'3_1^1$ band at 296 K*

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(Received 2 June 2008; revised manuscript received 25 January 2010)

This paper computes the rotational energy levels of the HCO $\tilde{B}^2A'$–$\tilde{X}^2A'$ transition, especially, the higher values of the rotational quantum numbers $N_{K_aK_c}$ and K_a, with the rotational constants which are obtained via B3LYP method with 6-311G basis set, and the results show that the calculated frequencies using the computed vibration–rotation energy levels are in reasonable agreement with the data from the experiment. Meanwhile, the line intensities of HCO are first reported, the results are of significance for the studying HCO.

Keywords: rotational energy levels, line intensities, vibration–rotation energy level, frequency
PACC: 3310E, 3320E, 3270

1. Introduction

The formal radical, HCO, is one of the most important organic radicals.[1] It plays an important role in the oxidation of hydrocarbons in combustion processes, in clean and polluted atmosphere.[1−9] Owing to the fundamental chemical significance of HCO, it has become the main subject of a large number of experimental and theoretical investigations. The vibration–rotation energy levels and the spectroscopic constants of HCO with the ASYTOP programme or a fully *ab initio* calculation have been discussed,[1−3,10−16] however, the vibration–rotation energy levels of the higher values of the rotational quantum numbers $J_{K_aK_c}$ and K_a, have not been reported, and the line intensities of HCO have not been investigated. In this paper, the HCO $\tilde{B}^2A'$–$\tilde{X}^2A'$ 3_1^1 transition is studied.

We provide a method based on Wang equation[17] for calculating rotational energy levels of HCO, and using calculated vibration–rotation energy levels, the computed frequencies are in very good agreement with the observed values in far infrared spectrum in most cases. With the calculated frequencies and the total internal partition function, we first report intensities of HCO, and present the simulated absorption spectra of the $\tilde{B}^2A'$–$\tilde{X}^2A'$ 3_1^1 band of HCO at 296 K.

2. Calculation of the rotational energy levels

The energy level value of a given rotational state for an asymmetric rotor is based on Wang:[17]

$$F(J_\tau) = \frac{1}{2}(B+C)J(J+1) + \left[A - \frac{1}{2}(B+C)\right]W_\tau, \quad (1)$$

where A, B and C are the rotational constants, W_τ is one of the $2J+1$ roots of the complex secular determinant, which can be factored into four algebraic equations to obtain the values of W_τ. And at present, the algebraic equations have been obtained by Nielsen[18] and Dennison group[19] for the levels J from $J = 0$ to $J = 11$. Thus the value of W_τ is the key to calculate the energy value of a given rotational state for an asymmetry top such as HCO (Generally, a rotational level is denoted by quantum numbers $N_{K_aK_c}$ for HCO). Now, the W_τ's are given below for $J = 11$ in the $\tilde{B}^2A(001)$ upper state of HCO: $W_{+11} = W_{+10} = 11^2$; $W_{+9} = W_{+8} = 10^2$; $W_{+7} = W_{+6} = 9^2$; $W_{+5} = W_{+4} = 64 = 8^2$; $W_{-10} = 0.994362$; $W_{-8} = 4 = 2^2$; $W_{+3} = W_{+2} = 49 = 7^2$; $W_{+1} = W_0 = 36 = 6^2$; $W_{-1} = W_{-2} = 25 = 5^2$; $W_{-11} = -0.0000156346$; $W_{-9} = 1.00563$; $W_{-3} = W_{-4} = 16 = 4^2$; $W_{-5} = W_{-6} = 9 = 3^2$; $W_{-7} = 4.00001 \approx 2^2$. The above results show that W_τ's are approximately equal to K_a^2

*Project supported by the National Natural Science Foundation of China (Grant No. 10676025).
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except for W_{-J}, W_{-J+1} and W_{-J+2}. Such phenomena also can be found in the levels J from $J = 0$ to $J = 10$ of the 3_1^1 band, which is determined by the near-prolate asymmetric rotor structure of HCO. Thus, for $J > 11$ of the band, the values of K_a^2 can be instead of those of W_τ except for W_{-J}, W_{-J+1} and W_{-J+2}.

The above computed rotational energy levels of HCO are considered as a rigid molecule. However, HCO is not completely rigid but slightly distorted due to its rotation. In order to resolve the problem of centrifugal distortion, it is necessary to consider the degree of asymmetry of a rotor. And the degree of its asymmetry is quantified by the asymmetry parameter[20] κ with

$$\kappa = \frac{2B - A - C}{A - C}. \tag{2}$$

The values of κ is in the range of -1–$+1$, it is equal to -1 for a prolate ($B = C$) and –1 for an oblate ($A = B$) with values near 0 for highly asymmetric rotors. There are the rotational constants, A, B and C of HCO in Table 1.

Table 1. Rotational parameters (cm^{-1}) of the HCO $\tilde{X}(^2A')$ and $\tilde{B}(^2A')$ state from the literature.

	[a]000[14]	[a]001[c]	[a]010[15]	[a]002[1]	[a]031[13]	[a]050[5]	[b]000[3]
A	24.3296015	26.5149	24.22469	28.39	25.84	23.73	15.976
B	1.4939571	1.44154	1.4823	1.50007	1.4605	1.427	1.19351
C	1.3986631	1.3425	1.38704	1.38982	1.3605	1.340	1.10769

[a] Rotational parameters (cm^{-1}) of the HCO $\tilde{X}(^2A')$ state, [b] Rotational parameters (cm^{-1}) of the HCO $\tilde{B}(^2A')$ state, [c] present work.

The following calculated values are the asymmetry parameter κ of the HCO, depending on the above rotational constants: $k = -0.9916886$; $k = -0.991462589$; $k = -0.99145$; $k = -0.991830$; $k = -0.99222873$; $k = -0.98845598$; $k = -0.99965879$. These data show that the degree of asymmetry of HCO is very small, thus the terms caused by the centrifugal forces of the rotation can be computed based on those of the prolate symmetric rotor.

Owing to the structure of a near-prolate asymmetric molecule of HCO, its doublet electronic state, with a net unpaired electron spin of $S = 1/2$, means that a rotational level is split via spin–rotation interaction into two components with resultant angular momentum $N_{K_aK_c} = J \pm 1/2$, thus the spin–rotation term must be considered, which come from the Ref. [16].

The formula of a rotational energy level of HCO is given below via the above rotational analysis:

$$F(N_\tau, J) = \frac{1}{2}(B + C)N(N + 1) + \left[A - \frac{1}{2}(B + C)\right] W_\tau - \Delta_N N^2(N + 1) - \Delta_{NK} N(N + 1)K^2 - \Delta_K K^4 - \frac{1}{2}\left[J(J + 1) - \frac{3}{4}\right]\left[a_0 - a + \frac{3aK^2}{N(N + 1)} - \eta\frac{K^4}{N(N + 1)}\right], \tag{3}$$

where $a_0 = -(\varepsilon_{aa} + \varepsilon_{bb} + \varepsilon_{cc})/3$, $a_0 = -(2\varepsilon_{aa} + \varepsilon_{bb} + \varepsilon_{cc})/6$, the rotational constants A, B and C, are obtained via B3LYP method with 6-311G basis set, and the 3_1^1 band origin (1080.237 cm^{-1}) of $\tilde{A}^2X(001)$ ground vibration state is derived from the Gauss programme with B3LYP method with 6-311G(2d) basis set. Compared with the experimental values (1080.7618 cm^{-1}), the error is small. Meanwhile, for $\tilde{B}^2A(001)$ upper vibration state, these constants are from the work of Yin and Scott,[1] including the derived vibronic origin (39670.1 ± 0.4 cm^{-1}), the centrifugal distortion constants Δ_N, Δ_{NK}, Δ_K and the spin–rotation interaction parameters ε_{aa}, ε_{bb}, ε_{cc}. With the calculated the vibration–rotation energy levels, we computed the frequencies of the 3_1^1 band of HCO.

3. The intensities of the vibration–rotation line

Once the vibration–rotation energy levels and frequencies are computed, the spectral line intensities can be calculated with the computed total internal

partition function. Generally, there is an approximation method,[19−22] which is convenient to calculate the line intensities for a asymmetry top molecule. Owing to near-prolate asymmetric rotor structure of HCO, it is easy to obtain the vibration–rotation line intensities based on the equation of a prolate symmetric rotor according to the method. Meanwhile, all the vibrations of HCO give rise in principle to a, b-type transition.

Line intensities have been computed with the conventional formula:[23]

$$S^{\nu' J' K'}_{\nu'' J'' K''}(T) = \frac{8\pi^3}{3hc}\nu^{\nu' J' K'}_{\nu'' J'' K''}\frac{g_{\nu'' J'' K''}\exp\left(-\dfrac{E_{\nu'' J'' K''}}{\kappa T}\right)}{Q(T)}(\mu^{\nu'}_{\nu''})^2 H^{J' K'}_{J'' K''}\left[1-\exp\left(-\frac{hc\nu^{\nu' J' K'}_{\nu'' J'' K''}}{\kappa T}\right)\right], \quad (4)$$

where h and κ are the Planck and Boltzman constants, respectively, c is the vacuum velocity of light, $\nu^{\nu' J' K'}_{\nu'' J'' K''}$ is the frequencies of the transition (cm^{-1}), $Q(T)$ is the total internal partition function, $E_{\nu'' J'' K''}$ is the energy of the lower levels (cm^{-1}), $\mu^{\nu'}_{\nu''}$ is the transition dipole moment (Debye), and $H^{J' K'}_{J'' K''}$ is the Honl–London factor,[24,20] $g_{\nu'' J'' K''}$ is the total statistical weight of the lower state, which meets the following relationship: $g_{\nu'' J'' K''} = g_i * g_1$, where g_i is the nuclear spin degeneracy, g_1 is the degeneracy of the lower state. For HCO, the degeneracy of the lower state is $g_1 = 2J + 1$ for $K = 0$ and $g_1 = 2(2J + 1)$ for $K \neq 0$, and the nuclear spin degeneracy is $g_i = 2$. Here, the values of $E_{\nu'' J'' K''}$ and $\nu^{\nu' J' K'}_{\nu'' J'' K''}$ have been discussed in Section 2, the values of $\mu^{\nu'}_{\nu''}$ are from the work of Manaa and Yarkony,[25] the total internal partition function is computed according to the product approximation.[18−22,26]

4. Results and discussion

In the Table 2, compared with the experimental values for the $\tilde{B}^2A'$–$\tilde{X}^2A'3^1_1$ band of HCO, it can be seen that computed frequencies in most cases are in very good agreement with those derived from the experiment. The errors for both our calculated frequencies and those observed are less than 0.3 cm^{-1}. And the results indicate that the above rotational energy analysis is reasonable, so for the higher values of the rotational quantum numbers $N_{K_a K_c}$ and K_a, the rational energy levels can be computed. Most importantly, such as HNO, its structure are similar to that of HCO, the rotational energy levels of the molecule is calculated by Eq. (3). Such excellent agreements enhance our confidence in the calculation of the total internal partition function and line intensity of HCO at 296 K. And the total internal partition function is obtained with the asymmetric model.[18−22,26] Meanwhile, the method computing the line intensity was applied to the other asymmetric top molecules, such as NH_3, so the data of the line intensity of the 3^1_1 band at 296 K are reliable. However, with calculated frequencies and the total internal partition function, the intensities of HCO are computed firstly, thus, at present, no theoretical or experimental data are yet available for our comparison. The experimental spectra and simulated spectrum of the band of HCO at 296 K are shown in Fig. 1.

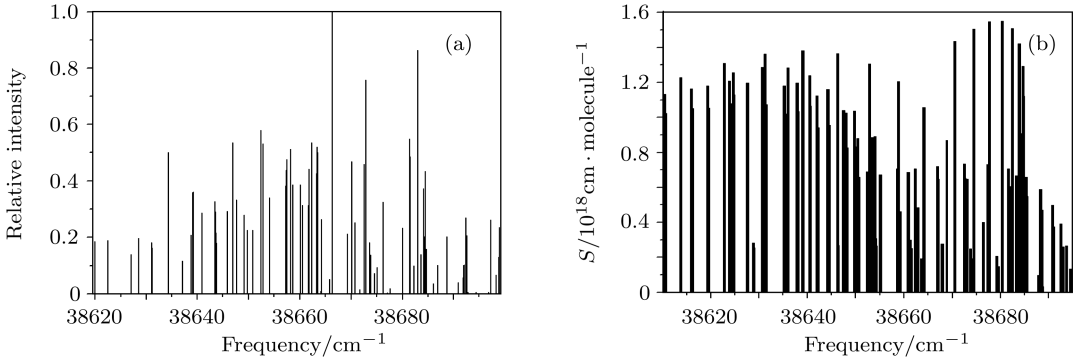


Fig. 1. The band $\tilde{B}^2A'$–$\tilde{X}^2A'3^1_1$ of HCO. Comparison of the experimental spectra from Ref. [1] with calculated spectra for 296 K.

Table 2. The frequency/cm^{-1} of the $\tilde{B}^2A' - \tilde{X}^2A'3_1^1$ band of HCO.

N'	Ka'	Kc'	J'	N"	Ka"	Kc"	J"	observed[a]	calculated	observed–calculated
1	0	1	0.5	0	0	0	0.5	38681.60	38681.64	–0.038
1	0	1	1.5	0	0	0	0.5	38681.60	38681.64	–0.038
2	0	2	1.5	1	0	1	0.5	38683.3	38683.31	–0.005
2	0	2	2.5	1	0	1	1.5	38683.3	38683.31	–0.005
3	0	3	2.5	2	0	2	1.5	38684.37	38684.36	0.011
3	0	3	3.5	2	0	2	2.5	38684.37	38684.36	0.011
4	0	4	3.5	3	0	3	2.5	38684.80	38684.80	0
4	0	4	4.5	3	0	3	3.5	38684.80	38684.80	0
5	0	5	4.5	4	0	4	3.5	38684.65	38684.62	0.027
5	0	5	5.5	4	0	4	4.5	38684.65	38684.62	0.027
6	0	6	5.5	5	0	5	4.5	38683.89	38683.83	0.059
6	0	6	6.5	5	0	5	5.5	38683.89	38683.83	0.059
7	0	7	6.5	6	0	6	5.5	38682.49	38682.42	0.069
7	0	7	7.5	6	0	6	6.5	38682.49	38682.42	0.069
8	0	8	7.5	7	0	7	6.5	38680.38	38680.39	–0.012
8	0	8	8.5	7	0	7	7.5	38680.51	38680.39	0.117
9	0	9	8.5	8	0	8	7.5	38677.86	38677.74	0.117
9	0	9	9.5	8	0	8	8.5	38677.86	38677.74	0.117
10	0	10	9.5	9	0	9	8.5	38674.64	38674.47	0.169
10	0	10	10.5	9	0	9	9.5	38674.64	38674.47	0.169
11	0	11	10.5	10	0	10	9.5	38670.81	38670.57	0.239
11	0	11	11.5	10	0	10	10.5	38670.81	38670.57	0.239
1	1	0	0.5	1	0	1	0.5	38694.52	38694.44	0.075
1	1	0	1.5	1	0	1	1.5	38693.67	38693.66	0.005
2	1	1	1.5	2	0	2	1.5	38693.07	38692.96	0.112
2	1	1	2.5	2	0	2	2.5	38692.47	38692.52	–0.053
3	1	2	2.5	3	0	3	2.5	38691.13	38691.05	0.082
3	1	2	3.5	3	0	3	3.5	38690.73	38690.74	–0.013
4	1	3	3.5	4	0	4	3.5	38688.57	38688.56	0.008
4	1	3	4.5	4	0	4	4.5	38688.34	38688.33	0.012
5	1	4	4.5	5	0	5	4.5	38685.58	38685.48	0.098
5	1	4	5.5	5	0	5	5.5	38685.37	38685.29	0.079
6	1	5	5.5	6	0	6	5.5	38681.96	38681.8	0.163
6	1	5	6.5	6	0	6	6.5	38681.69	38681.64	0.054
7	1	6	6.5	7	0	7	6.5	38677.63	38677.5	0.127
7	1	6	7.5	7	0	7	7.5	38677.46	38677.36	0.096
8	1	7	7.5	8	0	8	7.5	38672.77	38672.6	0.173
8	1	7	8.5	8	0	8	8.5	38672.6	38672.47	0.126
9	1	8	8.5	9	0	9	8.5	38667.3	38667.08	0.224
9	1	8	9.5	9	0	9	9.5	38667.18	38666.97	0.214
10	1	9	9.5	10	0	10	9.5	38661.25	38660.94	0.314
10	1	9	10.5	10	0	10	10.5	38661.12	38660.84	0.283

[a] the experimental data from the Ref. [1].

5. Conclusion

For the HCO $\tilde{B}^2A'(001)$–$\tilde{X}^2A'(001)$ band, the rotational energy levels are calculated based on the rotational constants obtained via B3LYP method with 6-311G basis set in Gauss programme. With the computed vibration–rotation energy levels, the calculated frequencies are in accordance with the available experimental

results. Most importantly, the method of the above rotational energy analysis is suitable for the other near-prolate and near-oblate asymmetric rotor molecules. Depending on the calculated vibration–rotation energy levels, frequencies and the total internal partition function, we first report the line intensities of the HCO $\tilde{B}^2A'(001)$–$\tilde{X}^2A'(001)$ transition.

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