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Saddle points of the potential energy surface for HCCF determined by an algebraic approach

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Abstract. The potential energy surface of the tetratomic molecule HCCF is determined by the U(4) algebraic method. The combination coefficients in the Hamiltonian are gotten from fitting the spectroscopic data. The molecular properties, such as, force constants and dissociation energies, are obtained in terms of the potential energy surface. A saddle point is also derived.

PACS. 02.20.Sv Lie algebras of Lie groups – 34.20.Cf Interatomic potentials and forces

1 Introduction

Molecular potential energy surfaces provide a foundation for understanding molecular phenomena. In recent years, various methods for studying potential energy surfaces of triatomic molecules have been developed [1–3]. Spectroscopy is the most accurate source of information on the potential energy surface, and it is now possible to obtain the reliable potential energy surface for small molecules from the observed spectra.

Information about potential energy surfaces has improved enormously in recent years, both from the analysis of experimental data and from ab initio calculations, but it is still a major task to gather this information into a functional representation which can be used for calculation.

The success of the interacting boson model of Arima and Iachello [4] has new interest in the study of many-body systems governed by algebraic Hamiltonians. In particular the properties of Hamiltonians with U(4) as the dynamical symmetry group have been investigated by several groups. It has been shown that algebraic technique are a powerful tool for the description of both time independent and time dependent phenomena [2,5–8].

Recently, the algebraic approach has been shown to be capable of providing an accurate description of the highly excited state spectra of triatomic molecules using a Hamiltonian containing a small number of parameters [2,9,10]. But the algebraic approach has no simple geometric interpretation, that is, it does not easily permit the resolution of the Hamiltonian into its kinetic and potential energy contributions. From the semiclassical limit of algebraic Hamiltonians, the explicit potential energy surface can be obtained.

Levine and coworkers have treated the potential energy surface of triatomic molecules using a U(2) algebraic model [11,12]. But the U(2) algebraic model is a one-dimensional model, and information about the bending motion can't be obtained using it. Recently, Zheng and Ding [2,3,13] have obtained the realistic potential energy surface of bent triatomic molecules and linear triatomic molecules using U(4) model, and they got good results. We have obtained the spectroscopy of the tetratomic molecules with the dynamical lie algebraic method [14]. In the present paper, we show how to obtain realistic potential energy surfaces of the tetratomic molecule HCCF using the U(4) algebraic model.

The organization of the work is as follows. In the second section we review algebraic Hamiltonian of the tetratomic molecule HCCF, and the expansion coefficients are given by fitting the spectroscopic data. Also we give the calculated vibrational energies and compare them with the experimental data. The third section gives the semiclassical Hamiltonian, while the potential energy surface is derived. Some molecular properties, such as the dissociation energies, force constants and saddle points, are found in section four. The final section give some discussions of the potential energy surface.

2 The Hamiltonian in creation and annihilation operators

In the tetratomic molecule HCCF, there are three independent vector coordinates, $\mathbf{r}_1$, $\mathbf{r}_2$ and $\mathbf{r}_3$ (we label the bonds as in Fig. 1), which can be thought of as three bonds. The general algebraic theory tells us that a quantization of these coordinates (and associated momenta) leads to the groups $\mathrm{G}_1 = \mathrm{U}_1(4)$, $\mathrm{G}_2 = \mathrm{U}_2(4)$

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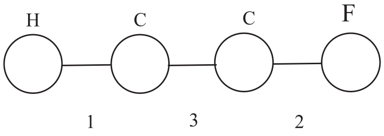

Fig. 1. The expression of the HCCF molecule.

and $G_3 = U_3(4)$, respectively. Then dynamical symmetric group of HCCF is [15]:

$$G = U_1(4) \otimes U_2(4) \otimes U_3(4). \tag{1}$$

Its corresponding subgroup chain is [14]

$$\begin{aligned} &U_1(4) \otimes U_2(4) \otimes U_3(4) \supset O_1(4) \otimes O_2(4) \otimes O_3(4) \\ &\quad \supset O_{12}(4) \otimes O_3(4) \supset O_{123}(4) \supset O_{123}(3) \supset O_{123}(2). \end{aligned} \tag{2}$$

The algebraic basis for this coupling scheme is characterized by the quantum numbers:

$$|[N_1],[N_2][N_3]p_1p_2(p_{12},q_{12})p_3(p,q)JM\rangle\,. \tag{3}$$

Here $[N_i]$ denotes the totally symmetric representation of $U_i(4)$ ($i = 1,2,3$), $(p_i, 0)$ denotes the symmetrical representation of $O_i(4)$ ($i = 1,2,3$), and (p_{12}, q_{12}) denotes the irreducible representation of $O_{12}(4)$. Here N_1, N_2, N_3 are fixed and the remaining quantum numbers p_1, p_2, p_3, p_{12}, q_{12}, p, q, J, M are precisely used to characterize the states of tetratomic molecule HCCF and its degeneracy. The relations between the group quantum numbers and the conventional quantum numbers of linear tetratomic molecule HCCF v_a, v_b, v_c, $v_d^{l_d}$, $v_e^{l_e}$ are:

$$\begin{aligned} &p_1 = N_1 - 2v_a, \quad p_2 = N_2 - 2v_c, \quad p_3 = N_3 - 2v_b, \\ &p_{12} = N_1 + N_2 - (2v_a + 2v_c + v_e), \quad q_{12} = l_e \\ &\quad p = N_1 + N_2 + N_3 - (2v_a + 2v_c + 2v_b + v_d + v_e), \\ &\quad q = l_d + l_e. \end{aligned}$$

The quantum numbers v_a, v_b, v_c denote the three local stretching modes; while $v_d^{l_d}$ and $v_e^{l_e}$ denote the two local bending modes. In the paper, we consider the coupling schemes (12)3, which emphasizes the coupling (12).

From the knowledge of the Lie algebra [14], the Hamiltonian of a tetratomic molecule HCCF is then expanded in terms of the Casimir operators of every subgroup in group chain (2), i.e. for linear tetratomic molecule HCCF, the expansion in terms of Casimir operators is

$$\begin{aligned} \hat{H} = E_0 + A_1\hat{C}_1 + A_2\hat{C}_2 + A_3\hat{C}_3 + A_{12}\hat{C}_{12} + A_{123}\hat{C}_{123} \\ + \lambda_{12}\hat{M}_{12} + \lambda_{23}\hat{M}_{23} + \lambda_{13}\hat{M}_{13}. \end{aligned} \tag{4}$$

Where A_1, A_2, A_3, A_{12}, A_{123}, λ_{12}, λ_{13}, λ_{23} are expansion coefficients, and they can be determined by spectroscopic data

$$C_i(i = 1,2,3) = D_i^2 + J_i^2 \tag{5}$$

is the Casimir operator of group $O_i(4)$ ($i = 1,2,3$);

$$\begin{aligned} C_{ij} &= C_{ij}^{(1)} + 2C_{ij}^{(2)} \\ &= (D_i + D_j)^2 + (J_i + J_j)^2 + 2[(D_i + D_j)(J_i + J_j)] \end{aligned} \tag{6}$$

is the Casimir operator of $O_i(4) \oplus O_j(4)$ ($i,j = 1,2,3$);

$$C_{123} = (D_1 + D_2 + D_3)^2 + (J_1 + J_2 + J_3)^2 \tag{7}$$

is the Casimir operator of $O_1(4) \oplus O_2(4) \oplus O_3(4)$ (D_i is the dipole operator, J_i is the angular momentum operator). M_{12}, M_{13}, M_{23} are the Majorana operator [14].

Table 1. The fitting parameters of C_2HF (all parameters are in cm^{-1}, except N_1, N_2, N_3 which are dimensionless).

N_1	43
N_2	113
N_3	137
A_1	−0.18512540(+2)
A_2	−0.22113612(+1)
A_3	−0.40846059(+1)
A_{12}	0.13254586(+1)
A_{123}	−0.99038659(+1)
λ_{12}	0.13407230(+1)
λ_{13}	−0.60777340(−3)
λ_{23}	0.18408663(−3)

According to the second quantization theory, the operators $J_{iu}^{(1)}$ and $D_{iu}^{(1)}$ can be expressed by creation and annihilation operators. The explicit representations of the dipole operators and angular momenta operators are

$$J_{iu}^{(1)} = \sqrt{2}\big[\pi_i^+ \times \tilde{\pi}_i\big]_u^{(1)} \tag{8}$$

$$D_{iu}^{(1)} = \big[\pi_i^+ \times \tilde{\sigma}_i + \sigma_i^+ \times \tilde{\pi}_i\big]_u^{(1)}. \tag{9}$$

Here, as usual, $J_{iu}^{(1)}(D_{iu}^{(1)})$ represents the u-component of rank-1 spherical tensor about bond i, the M_{12}, M_{13}, M_{23} are as follows

$$\begin{aligned} M_{13} = &\big[\pi_1^+ \times \sigma_3^+ - \sigma_1^+ \times \pi_3^+\big]^{(1)} \cdot \big[\tilde{\pi}_1 \times \tilde{\sigma_3} - \tilde{\sigma_1} \times \tilde{\pi}_3\big]^{(1)} \\ &+ 2\big[\pi_1^+ \times \pi_3^+\big]^{(1)} \cdot \big[\tilde{\pi}_1 \times \tilde{\pi}_3\big]^{(1)}, \\ M_{12} = &\big[\pi_1^+ \times \sigma_2^+ - \sigma_1^+ \times \pi_2^+\big]^{(1)} \cdot \big[\tilde{\pi}_1 \times \tilde{\sigma_2} - \tilde{\sigma_1} \times \tilde{\pi}_2]^{(1)} \\ &+ 2[\pi_1^+ \times \pi_2^+]^{(1)} \cdot [\tilde{\pi}_1 \times \tilde{\pi}_2\big]^{(1)}, \\ M_{23} = &\big[\pi_2^+ \times \sigma_3^+ - \sigma_2^+ \times \pi_3^+\big]^{(1)} \cdot \big[\tilde{\pi}_2 \times \tilde{\sigma_3} - \tilde{\sigma_2} \times \tilde{\pi}_3\big]^{(1)} \\ &+ 2\big[\pi_2^+ \times \pi_3^+\big]^{(1)} \cdot \big[\tilde{\pi}_2 \times \tilde{\pi}_3\big]^{(1)}. \end{aligned} \tag{10}$$

We can find the physical meaning of the Casimir in [15]. In order to get the vibrational states, we must calculate eigenvalues of the Hamiltonian (4), or in other words, we must calculate the eigenvalues of Casimir operators with the basis (3). In HCCF the vibron numbers N_1, N_2 and N_3 are taken to be 43, 113 and 137. We fit 71 observed data, which come from literature [16], using the least-square procedure. Fitting coefficient values are listed in Table 1. The fitting rms is 4.80 cm^{-1}. Partial calculated vibrational levels of HCCF are listed in Table 2, together with the experimental data [16].

Table 2. The calculated vibrational levels for HCCF (cm^{-1}). $\Delta = Cal. - Exp.$, $\delta = 100^{*}(Cal. - Exp.)/Exp.$

v_1, v_2, v_3	$v_4^{l_4}, v_5^{l_5}$	Exp. [20]	this paper	Δ	δ
0 0 0	0^0 2^0	732.08	738.62	6.54	0.894
0 0 0	1^1 1^{-1}	949.03	948.90	−0.13	−0.014
0 0 0	1^{-1} 1^1	952.67	958.28	5.61	0.589
0 0 1	0^0 0^0	1061.44	1061.18	−0.26	−0.025
0 0 0	2^0 0^0	1155.59	1157.72	2.13	0.185
0 1 0	0^0 0^0	2239.20	2241.17	1.97	0.088
1 0 0	0^0 0^0	3356.97	3351.27	−5.70	−0.170
0 0 0	0^0 4^0	1466.83	1466.33	−0.50	−0.034
0 0 1	0^0 2^0	1799.71	1800.84	1.13	0.063
0 0 1	1^1 1^{-1}	2011.03	2006.80	−4.50	−0.224
0 0 1	1^{-1} 1^1	2014.96	2015.88	0.92	0.046
0 0 0	3^1 1^{-1}	2100.42	2100.27	−0.15	−0.007
0 0 2	0^0 0^0	2108.13	2106.56	−1.57	−0.075
0 0 0	3^{-1} 1^1	2108.67	2113.54	4.87	0.231
0 0 1	2^0 0^0	2211.61	2210.98	−0.63	−0.028
0 0 0	4^0 0^0	2303.48	2309.57	6.09	0.264
0 1 0	0^0 2^0	2937.77	2939.57	1.80	0.061
0 1 0	1^1 1^{-1}	3166.02	3166.44	0.42	0.013
0 1 0	1^{-1} 1^1	3170.92	3171.48	0.56	0.018
0 1 1	0^0 0^0	3300.53	3294.43	−6.10	−0.185
0 1 0	2^0 0^0	3384.76	3391.02	6.26	0.185
1 0 1	0^0 0^0	4414.42	4411.60	−2.82	−0.064
0 2 0	0^0 0^0	4464.32	4458.63	−5.69	−0.127
0 0 2	0^0 2^0	2848.89	2854.30	5.41	0.190
0 0 3	0^0 0^0	3142.62	3150.24	7.62	0.242
0 0 1	4^0 0^0	3351.73	3354.90	3.17	0.095
0 1 1	1^1 1^{-1}	4228.92	4232.26	3.34	0.079
0 1 1	1^{-1} 1^1	4232.52	4241.14	8.62	0.204
0 1 2	0^0 0^0	4345.26	4338.87	−6.39	−0.147
0 1 1	2^0 0^0	4438.18	4436.36	−1.82	−0.041
1 0 2	0^0 0^0	5459.69	5463.12	3.43	0.063
1 2 0	2^0 0^0	5606.60	5600.62	−5.98	−0.107
1 1 1	0^0 0^0	6650.09	6652.40	2.31	0.035
0 0 4	0^0 0^0	4165.86	4171.10	5.24	0.126
1 0 3	0^0 0^0	6491.99	6490.97	−1.02	−0.016
1 0 1	4^0 0^0	6641.98	6638.04	−3.94	−0.059
0 2 0	4^0 0^0	6732.73	6736.64	3.91	0.058
0 1 2	4^0 0^0	6603.30	6603.96	0.66	0.010
0 0 0	0^0 1^1	366.64	367.02	0.38	0.103
0 0 0	1^1 0^0	583.70	583.16	−0.54	−0.092
0 0 0	1^1 2^0	1315.60	1316.86	1.26	0.096
0 0 0	1^{-1} 2^2	1322.24	1317.79	−4.45	−0.336
0 0 1	0^0 1^1	1431.34	1428.88	−2.46	−0.172
0 0 0	2^0 1^1	1523.44	1525.68	2.24	0.147
0 0 1	1^1 0^0	1642.77	1640.13	−2.64	−0.161
0 0 0	3^1 0^0	1735.37	1737.47	2.10	0.121
0 1 0	1^1 0^0	2816.16	2820.33	4.17	0.148
0 0 1	0^0 3^1	2170.48	2164.98	−5.50	−0.253
0 0 2	0^0 1^1	2479.66	2477.88	−1.78	−0.072
0 0 1	2^0 1^1	2581.50	2579.56	−1.94	−0.075
0 0 2	1^1 0^0	2687.33	2679.88	−7.45	−0.277
0 0 1	3^1 0^0	2788.30	2786.55	−1.75	−0.063
0 1 0	3^1 0^0	3959.42	3966.77	7.35	0.186
2 0 0	1^1 0^0	7149.29	7150.51	1.22	0.017
0 0 3	0^0 1^1	3518.64	3517.94	−0.70	−0.020
0 0 3	1^1 0^0	3718.70	3720.28	1.58	0.042
0 0 1	4^0 1^1	3725.03	3725.60	0.57	0.015
0 0 2	3^1 0^0	3828.54	3818.92	−9.62	−0.251
0 0 1	5^1 0^0	3927.63	3925.76	−1.87	−0.048
0 1 2	0^0 1^1	4700.39	4703.51	3.12	0.066
0 2 1	0^0 1^1	5865.79	5864.10	−1.69	−0.029
0 0 4	0^0 1^1	4540.52	4537.89	−2.63	−0.058
0 0 4	1^1 0^0	4741.33	4741.15	−0.18	−0.004
0 0 3	3^1 0^0	4854.04	4852.66	−1.38	−0.029
0 0 0	0^0 2^2	735.58	736.76	1.18	0.160
0 0 0	1^1 1^1	951.20	950.43	−0.77	−0.081
0 0 1	0^0 2^2	1803.43	1799.16	−4.27	−0.237
0 0 0	2^0 2^2	1893.64	1893.93	0.29	0.015
0 0 1	1^1 1^1	2013.52	2008.08	−5.44	−0.270
0 0 0	3^1 1^1	2104.48	2103.40	−1.08	−0.051
0 0 2	0^0 2^2	2852.60	2852.83	0.23	0.008
0 1 1	1^1 1^1	4231.51	4233.46	1.95	0.046
2 2 0	1^1 1^{-1}		11937.71		
3 1 0	0^0 2^0		12638.29		
4 1 0	0^0 0^0		14840.12		
5 0 0	0^0 0^0		15463.03		
0 1 0	0^0 5^1		4024.80		
0 1 0	2^0 3^1		4475.57		
2 0 0	0^0 3^1		7694.91		
2 0 1	0^0 1^1		8009.51		
0 0 0	3^1 6^0		3875.07		
0 0 4	0^0 1^1		4473.60		
0 1 0	5^{-1} 2^2		5828.61		
0 1 0	5^3 2^{-2}		5836.80		
1 0 1	4^0 1^1		7010.40		
1 1 0	2^2 3^{-1}		7827.22		
0 3 0	2^0 1^1		8151.27		
2 0 0	3^1 2^0		9030.62		
1 2 0	1^1 2^0		9062.45		
2 0 2	0^0 1^1		9097.33		
2 0 1	2^0 1^1		9146.02		
2 0 0	4^2 1^{-1}		9206.12		
1 2 0	2^2 1^{-1}		9304.81		
1 2 1	1^1 0^0		9406.87		
2 1 0	0^0 3^1		9910.04		
2 1 0	2^0 1^1		10307.37		
1 3 0	1^1 0^0		10550.64		
3 0 0	2^0 1^1		11106.27		
3 0 0	2^2 1^{-1}		11191.07		
3 0 1	1^1 0^0		11368.19		
3 1 0	0^0 1^1		12259.74		
4 0 0	1^1 0^0		13196.77		

$$
\begin{aligned}
\hat{H} = E_0 &+ A_1\Big\{\Big[\big(\pi_1^+ \times \tilde{\sigma_1} + \sigma_1^+ \times \tilde{\pi}_1\big)_k^{(1)}\Big]^2 + \Big[\sqrt{2}\big(\pi_1^+ \times \tilde{\pi}_1\big)_k^{(1)}\Big]^2\Big\} \\
&+ A_2\Big\{\Big[\big(\pi_2^+ \times \tilde{\sigma_2} + \sigma_2^+ \times \tilde{\pi}_2\big)_k^{(1)}\Big]^2 + \Big[\sqrt{2}\big(\pi_2^+ \times \tilde{\pi}_2\big)_k^{(1)}\Big]^2\Big\} + A_3\Big\{\Big[\big(\pi_3^+ \times \tilde{\sigma_3} + \sigma_3^+ \times \tilde{\pi}_3\big)_k^{(1)}\Big]^2 + \Big[\sqrt{2}\big(\pi_3^+ \times \tilde{\pi}_3\big)_k^{(1)}\Big]^2\Big\} \\
&+ A_{12}\Big\{\Big[\big(\pi_1^+ \times \tilde{\sigma_1} + \sigma_1^+ \times \tilde{\pi}_1\big)_k^{(1)}\Big]^2 + \Big[\sqrt{2}\big(\pi_1^+ \times \tilde{\pi}_1\big)_k^{(1)}\Big]^2 + \Big[\big(\pi_2^+ \times \tilde{\sigma_2} + \sigma_2^+ \times \tilde{\pi}_2\big)_k^{(1)}\Big]^2 + \Big[\sqrt{2}\big(\pi_2^+ \times \tilde{\pi}_2\big)_k^{(1)}\Big]^2 \\
&\qquad + 2\Big(\Big[\big(\pi_1^+ \times \tilde{\sigma_1} + \sigma_1^+ \times \tilde{\pi}_1\big)_k^{(1)}\Big] \cdot \Big[\big(\pi_2^+ \times \tilde{\sigma_2} + \sigma_2^+ \times \tilde{\pi}_2\big)_k^{(1)}\Big] + \Big[\sqrt{2}\big(\pi_1^+ \times \tilde{\pi}_1\big)_k^{(1)}\Big] \cdot \Big[\sqrt{2}\big(\pi_2^+ \times \tilde{\pi}_2\big)_k^{(1)}\Big]\Big)\Big\} \\
&+ A_{123}\Big\{\Big[\big(\pi_1^+ \times \tilde{\sigma_1} + \sigma_1^+ \times \tilde{\pi}_1\big)_k^{(1)}\Big]^2 + \Big[\sqrt{2}\big(\pi_1^+ \times \tilde{\pi}_1\big)_k^{(1)}\Big]^2 + \Big[\big(\pi_2^+ \times \tilde{\sigma_2} + \sigma_2^+ \times \tilde{\pi}_2\big)_k^{(1)}\Big]^2 + \Big[\sqrt{2}\big(\pi_2^+ \times \tilde{\pi}_2\big)_k^{(1)}\Big]^2 \\
&\qquad + \Big[\big(\pi_3^+ \times \tilde{\sigma_3} + \sigma_3^+ \times \tilde{\pi}_3\big)_k^{(1)}\Big]^2 + \Big[\sqrt{2}\big(\pi_3^+ \times \tilde{\pi}_3\big)_k^{(1)}\Big]^2 + 2\Big(\Big[\big(\pi_1^+ \times \tilde{\sigma_1} + \sigma_1^+ \times \tilde{\pi}_1\big)_k^{(1)}\Big] \cdot \Big[\big(\pi_2^+ \times \tilde{\sigma_2} + \sigma_2^+ \times \tilde{\pi}_2\big)_k^{(1)}\Big] \\
&\qquad + \Big[\sqrt{2}\big(\pi_1^+ \times \tilde{\pi}_1\big)_k^{(1)}\Big] \cdot \Big[\sqrt{2}\big(\pi_2^+ \times \tilde{\pi}_2\big)_k^{(1)}\Big] + \Big[\big(\pi_1^+ \times \tilde{\sigma_1} + \sigma_1^+ \times \tilde{\pi}_1\big)_k^{(1)}\Big] \cdot \Big[\big(\pi_2^+ \times \tilde{\sigma_2} + \sigma_2^+ \times \tilde{\pi}_2\big)_k^{(1)}\Big] \\
&\qquad + \Big[\sqrt{2}\big(\pi_1^+ \times \tilde{\pi}_1\big)_k^{(1)}\Big] \cdot \Big[\sqrt{2}\big(\pi_2^+ \times \tilde{\pi}_2\big)_k^{(1)}\Big] + 2\Big(\Big[\big(\pi_1^+ \times \tilde{\sigma_1} + \sigma_1^+ \times \tilde{\pi}_1\big)_k^{(1)}\Big] \cdot \Big[\big(\pi_3^+ \times \tilde{\sigma_3} + \sigma_3^+ \times \tilde{\pi}_3\big)_k^{(1)}\Big] \\
&\qquad + \Big[\sqrt{2}\big(\pi_2^+ \times \tilde{\pi}_2\big)_k^{(1)}\Big] \cdot \Big[\sqrt{2}\big(\pi_3^+ \times \tilde{\pi}_3\big)_k^{(1)}\Big]\Big)\Big\} \\
&+ \lambda_{12}\Big\{\big[\pi_1^+ \times \sigma_2^+ - \sigma_1^+ \times \pi_2^+\big]^{(1)} \cdot \big[\tilde{\pi}_1 \times \tilde{\sigma_2} - \tilde{\sigma_1} \times \tilde{\pi}_2\big]^{(1)} + 2\big[\pi_1^+ \times \pi_2^+\big]^{(1)} \cdot \big[\tilde{\pi}_1 \times \tilde{\pi}_2\big]^{(1)}\Big\} \\
&+ \lambda_{23}\Big\{\big[\pi_2^+ \times \sigma_3^+ - \sigma_2^+ \times \pi_3^+\big]^{(1)} \cdot \big[\tilde{\pi}_2 \times \tilde{\sigma_3} - \tilde{\sigma_2} \times \tilde{\pi}_3\big]^{(1)} + 2\big[\pi_2^+ \times \pi_3^+\big]^{(1)} \cdot \big[\tilde{\pi}_2 \times \tilde{\pi}_3\big]^{(1)}\Big\} \\
&+ \lambda_{13}\Big\{\big[\pi_1^+ \times \sigma_3^+ - \sigma_1^+ \times \pi_3^+\big]^{(1)} \cdot \big[\tilde{\pi}_1 \times \tilde{\sigma_3} - \tilde{\sigma_1} \times \tilde{\pi}_3\big]^{(1)} + 2\big[\pi_1^+ \times \pi_3^+\big]^{(1)} \cdot \big[\tilde{\pi}_1 \times \tilde{\pi}_3\big]^{(1)}\Big\}
\end{aligned}
\tag{11}
$$

Putting equations (5–10) into equation (4), we shall get the molecular algebraic Hamiltonian in spherical operators version:

see equation (11) *above.*

3 Potential energy surface

3.1 The classical Hamiltonian

It is obvious that the Hamiltonian (11), expressed by creation and annihilation operators, does not have an explicit kinetic and potential form. However, it is possible to return to the potential energy surface by a direct study of the inverse problem. The geometric space of an algebraic structure is called, in mathematical terms, cosset space. This cosset space is intimately related to the starting algebraic structure and leads to the classical limits of Boson operators. In one such limit, this different realization of the system's quantum states is called a coherent state realization [17].

In the U(4) case, the coherent states have the form [13]

$$|[N],\xi\rangle = \frac{1}{\sqrt{N!}}\left[\left(1+|\xi|^2\right)^{-1/2}\left(\sigma^+ + \xi\cdot\pi^+\right)\right]^N|0\rangle \tag{12}$$

and the complex number ξ represents the vector vibron in phase space. The classical limit of the algebraic Hamiltonian (11) is then defined as the expectation value of H over the coherent state

$$H_{cl}(\xi,\xi^*) = \langle[N],\xi|H|[N],\xi\rangle\,. \tag{13}$$

For calculating equation (13), we must calculate every term in equation (11). For example, the expectation value of some terms in equation (11) are as follows,

$$
\begin{aligned}
\langle[N],\xi\left|\sigma^+\pi\right|[N],\xi\rangle &= N\xi^*\sqrt{1-\xi^*\cdot\xi} \\
\langle[N],\xi\left|\sigma^+\sigma\right|[N],\xi\rangle &= N\xi^*\cdot\xi \\
\langle[N],\xi\left|(\sigma^+\pi)^2\right|[N],\xi\rangle &= N(N-1)(\xi^*)^2(1-\xi^*\cdot\xi).
\end{aligned}
\tag{14}
$$

We can introduce a more familiar form of the Hamiltonian by considering the canonical transformation

$$\xi_i = \frac{1}{\sqrt{2}}(\mathbf{q}_i+j\mathbf{p}_i);\quad \xi_i^* = \frac{1}{\sqrt{2}}(\mathbf{q}_i-j\mathbf{p}_i)\quad (j=\sqrt{-1}). \tag{15}$$

Taking equations (14, 15) into equation (13), we obtain the classical Hamiltonian H_{cl}.

3.2 Potential energy surface

The canonical coordinates and momenta satisfy Hamilton's canonical equations

$$\dot{\mathbf{q}}_i = \frac{\partial H_{cl}}{\partial \mathbf{p}_i},\quad \dot{\mathbf{p}}_i = -\frac{\partial H_{cl}}{\partial \mathbf{q}_i}. \tag{16}$$

The potential energy surface is defined as

$$V(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3) = H_{cl}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3;\mathbf{p}_1=0,\mathbf{p}_2=0,\mathbf{p}_3=0). \tag{17}$$

We use the transformation between bond coordinates and classical coordinates [2]

$$q_i^2 = e^{-\beta_i(r_i-r_{ie})}\quad (i=1,2,3) \tag{18}$$

$$\alpha_i = \frac{2\pi c v_i}{\sqrt{-\left\{2(A_{12}+A_{123})N_1N_2 + 2(A_{i3}+A_{123})N_iN_3 - \frac{3}{2}\lambda_{12}N_1N_2 - \frac{3}{2}\lambda_{i3}N_iN_3\right\}\left(\frac{u_1}{r_{ie}^2}+\frac{u_2}{r_{3e}^2}+u_3\left(\frac{1}{r_{ie}^2}+\frac{1}{r_{3e}^2}+\frac{2}{r_{ie}r_{3e}}\right)\right)}} \quad (i=1,2). \tag{25}$$

where r_i is the ith bond coordinate, r_{ie} is the equilibrium bond length, and β_i is a spectral parameter. The value of β_i is calculated with the formula [18]:

$$\beta_i = \sqrt{\frac{2\pi^2 c u_{iA}}{D_{ie}}}\, w_{ie}. \tag{19}$$

w_{ie}, u_{iA}, D_{ie} has the usual meaning as in reference [18]. α_i is the parameter which is given in the next section; θ_i is the bond angle. Here we introduce the transformation:

$$\begin{aligned}\mathbf{a}_1\cdot\mathbf{a}_3 &= \frac{1}{\cosh\alpha_1(\theta_1-\theta_{10})},\\ \mathbf{a}_2\cdot\mathbf{a}_3 &= \frac{1}{\cosh\alpha_2(\theta_2-\theta_{20})}.\end{aligned} \tag{20}$$

The value of $\mathbf{a}_1\cdot\mathbf{a}_2$ is determined by the relation of $\mathbf{q}_1$, $\mathbf{q}_2$, $\mathbf{q}_3$, where $\mathbf{a}_i$ is the unit vector along the vector $\mathbf{q}_i$, θ_i is the bond angle, θ_{i0} is the equilibrium bond angle. Taking equations (18–20) into equation (17), we can get the expression of the potential energy surface with the molecular bond coordinates.

Derivation of the parameters α_i

Within the Born-Oppenheimer approximation, the kinetic operator for bond angle is

$$T = -\frac{\hbar^2}{2}\sum_{ij} G_{ij}\frac{\partial^2}{\partial r_i \partial r_j} \tag{21}$$

and

$$\begin{aligned}G_{\theta_1\theta_1} &= \frac{u_1}{r_{1e}^2}+\frac{u_2}{r_{3e}^2}+u_3\left(\frac{1}{r_{1e}^2}+\frac{1}{r_{3e}^2}+\frac{2}{r_{1e}r_{3e}}\right)\\ G_{\theta_2\theta_2} &= \frac{u_4}{r_{2e}^2}+\frac{u_2}{r_{3e}^2}+u_3\left(\frac{1}{r_{2e}^2}+\frac{1}{r_{3e}^2}+\frac{2}{r_{21e}r_{3e}}\right).\end{aligned} \tag{22}$$

We know

$$\begin{aligned}k_{\theta_1\theta_1} &= \frac{(2\pi c v_1)^2}{G_{\theta_1\theta_1}} = \left.\frac{\partial^2 V}{\partial\theta_1^2}\right|_{r_1=r_{1e},r_2=r_{2e},r_3=r_{3e},\theta_1=\theta_{10},\theta_2=\theta_{20}}\\ &= -\Big\{2(A_{12}+A_{123})N_1N_2+2(A_{13}+A_{123})N_1N_3\\ &\quad -\frac{3}{2}\lambda_{12}N_1N_2-\frac{3}{2}\lambda_{13}N_1N_3\Big\}\alpha_1^2\\ k_{\theta_2\theta_2} &= \frac{(2\pi c v_2)^2}{G_{\theta_2\theta_2}} = \left.\frac{\partial^2 V}{\partial\theta_2^2}\right|_{r_1=r_{1e},r_2=r_{2e},r_3=r_{3e},\theta_1=\pi,\theta_2=\pi}\\ &= -\Big\{2(A_{12}+A_{123})N_1N_2+2(A_{23}+A_{123})N_2N_3\\ &\quad -\frac{3}{2}\lambda_{12}N_1N_2-\frac{3}{2}\lambda_{23}N_2N_3\Big\}\alpha_2^2\end{aligned} \tag{23}$$

and

$$(2\pi c v_i)^2 = k_{\theta_i\theta_i}G_{\theta_i\theta_i} \tag{24}$$

v_i is the bending frequency, and c is the light velocity. From equations (22–24), we obtain the expression for parameters $\alpha_1$and α_2

see equation (25) *above.*

4 Molecular properties

4.1 Force constants

We obtain the potential energy surface by using the semiclassical limit of algebraic Hamiltonians. So by using equations (17–25) some properties of the potential surface can be discussed. For simplicity, we only calculate the second order force constants in the present paper

$$\begin{aligned}k_{r_1r_1} &= \left.\frac{\partial^2 v}{\partial r_1^2}\right|_{r_1=r_{1e},r_2=r_{2e},r_3=r_{3e},\theta_1=\theta_{10},\theta_2=\theta_{20}}\\ &= -2A_1\beta_1^2N_1^2 + A_{12}\big(-2\beta_1^2N_1^2-2\beta_1^2N_1N_2\big)\\ &\quad +0.5\lambda_{12}\beta_1^2N_1N_2+0.5\lambda_{13}\beta_1^2N_1N_3\\ &\quad +A_{123}\big(-2\beta_1^2N_1^2-2\beta_1^2N_1N_2-2\beta_1^2N_1N_3\big)\\ k_{r_2r_2} &= \left.\frac{\partial^2 v}{\partial r_2^2}\right|_{r_1=r_{1e},r_2=r_{2e},r_3=r_{3e},\theta_1=\theta_{10},\theta_2=\theta_{20}}\\ &= -2A_2\beta_2^2N_2^2 + A_{12}\big(-2\beta_2^2N_2^2-2\beta_2^2N_1N_2\big)\\ &\quad +0.5\lambda_{12}\beta_2^2N_1N_2+0.5\lambda_{23}\beta_2^2N_2N_3\\ &\quad +A_{123}\big(-2\beta_2^2N_2^2-2\beta_2^2N_1N_2-2\beta_2^2N_2N_3\big)\\ k_{r_3r_3} &= \left.\frac{\partial^2 v}{\partial r_3^2}\right|_{r_1=r_{1e},r_2=r_{2e},r_3=r_{3e},\theta_1=\theta_{10},\theta_2=\theta_{20}}\\ &= -2A_3\beta_3^2N_3^2+0.5\lambda_{13}\beta_3^2N_1N_3+0.5\lambda_{23}\beta_3^2N_2N_3\\ &\quad +A_{123}\big(-2\beta_3^2N_3^2-2\beta_3^2N_1N_3-2\beta_3^2N_2N_3\big)\\ k_{\theta_1\theta_1} &= \left.\frac{\partial^2 v}{\partial\theta_1^2}\right|_{r_1=r_{1e},r_2=r_{2e},r_3=r_{3e},\theta_1=\theta_{10},\theta_2=\theta_{20}}\\ &= (-2A_{12}N_1N_2+A_{123}(-2N_1N_2-2N_1N_3)\\ &\quad +1.5\lambda_{12}N_1N_2+1.5\lambda_{13}N_1N_3)\alpha_1^2\\ k_{\theta_2\theta_2} &= \left.\frac{\partial^2 v}{\partial\theta_2^2}\right|_{r_1=r_{1e},r_2=r_{2e},r_3=r_{3e},\theta_1=\theta_{10},\theta_2=\theta_{20}}\\ &= (-2A_{12}N_1N_2+A_{123}(-2N_1N_2-2N_1N_3)\\ &\quad +1.5\lambda_{12}N_1N_2+1.5\lambda_{23}N_2N_3)\alpha_2^2.\end{aligned} \tag{26}$$

$$\begin{aligned}V(q_1,q_2,q_3) &= (A_1+A_{12}+A_{123})\left\{N_1^2(2-q_1^2)q_1^2\right\}+(A_2+A_{12}+A_{123})\left\{N_2^2(2-q_2^2)q_2^2\right\}+(A_3+A_{123})\left\{N_3^2(2-q_3^2)q_3^2\right\}\\ &+(2A_{12}+2A_{123})\left\{N_1N_2(2-q_1^2)^{\frac{1}{2}}(2-q_2^2)^{\frac{1}{2}}q_1q_2\right\}+2A_{123}\left\{N_1N_3(2-q_1^2)^{\frac{1}{2}}(2-q_3^2)^{\frac{1}{2}}q_1q_3+N_2N_3(2-q_2^2)^{\frac{1}{2}}(2-q_3^2)^{\frac{1}{2}}q_2q_3\right\}\\ &+\lambda_{12}\left(\frac{1}{4}N_1N_2\left(2-q_2^2\right)q_1^2+\frac{1}{4}N_1N_2\left(2-q_1^2\right)q_2^2-\frac{1}{2}N_1N_2\left[\left(2-q_1^2\right)\left(2-q_2^2\right)\right]^{\frac{1}{2}}q_1q_2\right)\\ &+\lambda_{13}\left(\frac{1}{4}N_1N_3\left(2-q_3^2\right)q_1^2+\frac{1}{4}N_1N_3\left(2-q_1^2\right)q_3^2-\frac{1}{2}N_1N_3\left[\left(2-q_1^2\right)\left(2-q_3^2\right)\right]^{\frac{1}{2}}q_1q_3\right)\\ &+\lambda_{23}\left(\frac{1}{4}N_3N_2\left(2-q_2^2\right)q_3^2+\frac{1}{4}N_3N_2\left(2-q_3^2\right)q_2^2-\frac{1}{2}N_3N_2\left[\left(2-q_3^2\right)\left(2-q_2^2\right)\right]^{\frac{1}{2}}q_3q_2\right)\end{aligned}\qquad(29)$$

Table 3. The force constants (aJ; Å; Rad) and the dissociation energy (eV) of HCCF.

The values of this work	Reference [1]
$k_{11} = 6.25795$	$k_{11} = 6.370$
$k_{22} = 6.4219$	$k_{33} = 16.341$
$k_{33} = 15.3966$	$k_{\theta_1\theta_1} = 0.251$
$k_{\theta_1\theta_1} = 0.251988$	
$k_{\theta_2\theta_2} = 0.917484$	
$D_e = 23.7915$	
$D_{e1} = 3.76336$	
$D_{e2} = 2.56634$	
$D_{e3} = 11.8096$	

4.2 Dissociation energy

It is obvious that at $r_1 \to r_{1e}$, $r_2 \to r_{2e}$ and $r_3 \to r_{3e}$ the potential energy surface has the global minimum, and the well depth at the minimum of the potential is

$$\begin{aligned}D_e = -(&A_1N_1^2+A_2N_2^2+A_3N_3^2+A_{12}(N_1+N_2)^2\\ &+A_{123}(N_1+N_2+N_3)^2).\end{aligned}\qquad(27)$$

The other stationary points of $V(r_1, r_2, r_3, \theta_1, \theta_2)$ are at $r_1 \to r_{1\infty}$, $r_2 \to r_{2\infty}$, $r_3 = r_{3e}$ or at $r_1 \to r_{1\infty}$, $r_2 = r_{2e}$, $r_3 \to r_{3\infty}$ and $r_1 = r_{1e}$, $r_2 \to r_{2\infty}$, $r_3 \to r_{3\infty}$ which are the three valleys where two bonds are fully extended and another bond is at its equilibrium position. The depth of the ith valley is $\hat{D}_{ei}$:

$$\begin{aligned}D_{e1} &= -(A_1N_1^2+A_{12}N_1^2+A_{123}N_1^2\\ &\quad+0.5\lambda_{12}N_1N_2+0.5\lambda_{13}N_1N_3)\\ D_{e2} &= -(A_2N_2^2+A_{12}N_2^2+A_{123}N_2^2\\ &\quad+0.5\lambda_{12}N_1N_2+0.5\lambda_{13}N_1N_3)\\ D_{e3} &= -(A_3N_3^2+A_{123}N_3^2+0.5\lambda_{13}N_1N_3+0.5\lambda_{23}N_2N_3).\end{aligned}\qquad(28)$$

The force constants and the dissociation energies are listed in Table 3 with the result of the other method [1].

4.3 Saddle points

In the paper, we discuss the saddle points of the potential energy surface. To reach this goal, we first need to obtain the stationary points of equation (17). At the same time, for mathematical simplicity, we consider the potential energy surface with equilibrium bond angles:

see equation (29) *above*.

The basic stationary points are

1. $\{q_1 = 0,\ q_2 = 0,\ q_3 = 0\}$. That is, $\{r_1 \to \infty,\ r_2 \to \infty,\ r_3 \to \infty\}$ when the transformation (18) are considered. This solution corresponds to the case in which the three bonds are completely broken, i.e., the molecule is dissociated;
2. $\{q_1 = 0,\ q_2 = 0,\ q_3 = 1\}$, $\{q_1 = 0,\ q_2 = 1,\ q_3 = 0\}$ and $\{q_1 = 1,\ q_2 = 0,\ q_3 = 0\}$. That is, $\{r_1 \to \infty,\ r_2 \to \infty,\ r_3 \to r_{3e}\}$ when transformation (18) are considered; $\{r_1 \to \infty,\ r_2 \to r_{2e},\ r_3 \to \infty\}$ and $\{r_1 \to r_{1e},\ r_2 \to \infty,\ r_3 \to \infty\}$ the three solutions correspond to the case of two bond fully extended and the other bond at its equilibrium position;
3. $\{q_1 = 1,\ q_2 = 1,\ q_3 = 1\}$. This solution corresponds to $\{r_1 \to r_{1e},\ r_2 \to r_{2e},\ r_3 \to r_{3e}\}$. It means that the potential-energy surface reaches the global minimum;
4. $\{q_1 = 0,\ q_2 = 1,\ q_3 = 1\}$, $\{q_1 = 1,\ q_2 = 1,\ q_3 = 0\}$ and $\{q_1 = 1,\ q_2 = 0,\ q_3 = 1\}$. That is, $\{r_1 \to \infty,\ r_2 \to r_{2e},\ r_3 \to r_{3e}\}$ when transformation (18) are considered, $\{r_1 \to r_{1e}, r_2 \to r_{2e}, r_3 \to \infty\}$ and $\{r_1 \to r_{1e},\ r_2 \to \infty,\ r_3 \to r_{3e}\}$. The three solutions correspond to the case of one bond extended and the other two bonds at their equilibrium.

The four cases above are trivial solutions of the equations for stationary points, and they have been discussed in detail in Sections 4.1 and 4.2. But they are not saddle points. For deriving the saddle points, first we should find the stationary points different from the above four cases, so we should solve the next equations

$$\frac{\partial V}{\partial q_1} = 0;\quad \frac{\partial V}{\partial q_2} = 0;\quad \frac{\partial V}{\partial q_3} = 0.\qquad(30)$$

Solving equations (30), we get some new points (q_1, q_2, q_3); in the next we will illustrate why the point is saddle point. We define the matrix A as followings:

$$A = \begin{vmatrix} a_{11} & a_{12} & a_{13}\\ a_{21} & a_{22} & a_{23}\\ a_{31} & a_{32} & a_{33}\end{vmatrix}$$

$$(a_{ij} = f''_{q_iq_j}(q_{10}, q_{20}, q_{30})\quad i,j = 1,2,3).\qquad(31)$$

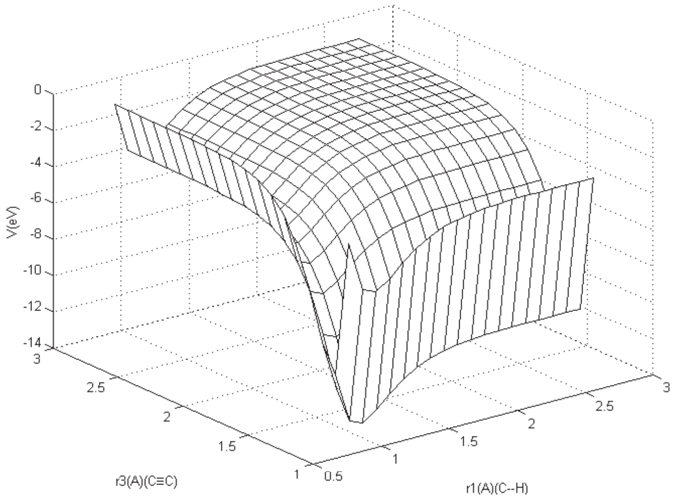

Fig. 2. The potential energy surface of stable C_2HF with r_1 and r$_3$ ($r_2 \rightarrow r_{2e}$).

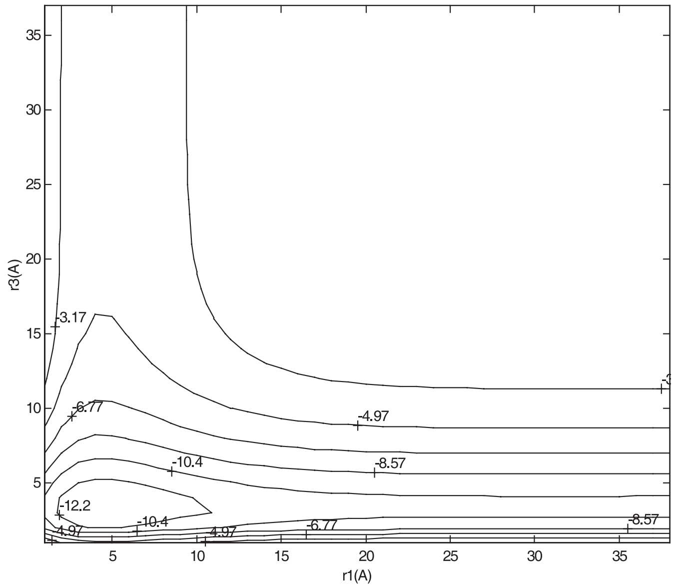

Fig. 3. The contours of stable C_2HF with r_1 and r_3 ($r_2 = r_{2e}$).

From the knowledge of [19], we know: when the matrix A is positive definite, (q_{10}, q_{20}, q_{30}) has a minimum at ($q_{10} > 0$, $q_{20} > 0$, $q_{30} > 0$); when the matrix A is negative definite, $V(q_1, q_2, q_3)$ has a maximum at ($q_{10} > 0$, $q_{20} > 0$, $q_{30} > 0$); when A is indefinite, $V(q_1, q_2, q_3)$ has no peak point at (q_{10}, q_{20}, q_{30}). As usual, a stationary point (q_{10}, q_{20}, q_{30}) at which V is neither maximum nor minimum may be a saddle point. If we get all the peak points and compare them, we can get the saddle points. With our own Fortran program we know at ($r_1 = 1.06445$ Å, $r_2 = 1.19855$ Å, $r_3 = 1.22924$ Å)

$$|a_{11}| > 0, \qquad \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} > 0, \qquad \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} < 0.$$

The Hessian A is indefinite. HCCF exits a saddle point.

5 Discussions

The potential energy surface is a four-dimensional figure if we don't consider the bond angles. For plotting the three dimensional figures, we suppose that one bond is at its equilibrium and the potential energy surface is changing with the other two bonds. In Figure 2, we suppose that the bond 2 is at its equilibrium and the potential energy surface changes with bond 1 and bond 3. Also in Figure 3 we plot the contours corresponding to Figure 2. With the analytical potential energy surface we got, we can discuss some chemical problems. This work is in progress.

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