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Algebraic Study of the Vibrational Levels and Potential Energy Surface of the Excited Electronic State (\tilde{C}^1A') for S_2O Xiao-yan Wang^{a*}, Shi-liang Ding^b, Jin-dong Xie^a, Peng-cheng Wang^a, Wei-gang Zhong^a*a.* Department of Radiology, Taishan Medical School, Taian 271000, China; *b.* School of Physics and Microelectronics, Shandong University, Ji'nan 250100, China

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The vibrational levels and potential energy surface of a stable structure for S_2O in the excited electronic states \tilde{C}^1A' were carried out with algebraic method. The vibrational spectra were obtained (with total quantum number $v=20$) by fitting 30 spectra data. The fitted rms (root mean square) error based on the Hamiltonian with 9 parameters was 2.40 cm^{-1} . The dissociation energy and force constant were also determined by the analytical potential energy surface. The method is proved to be effective by comparing these results with the experimental data.

Key words: S_2O , Energy level, Potential energy surface

I. INTRODUCTION

In recent years, theoretical studies of molecular spectra have been one of the most important methods. Scientists can get the rotation, vibration and electron energy level. With these knowledges, the distance between nucleus, vibration frequency, force constants, dissociation energy and the other data about the molecular geometry can be accurately determined.

S_2O is one important transient state product of chemical reaction. Since the initial report in 1933 [1], the geometry of S_2O molecular has suffered a long history of mistaken identity and muddled spectral interpretation because of the mistaken measurement about the matching of S to O (1:1) in chemistry. The work of Meschi and Myers in the late 1950's using mass and microwave spectroscopic techniques proved conclusively the presence of a triatomic molecule and denied the experience formula (SO). Recently astronomer has proved S_2O 's existence in interstellar atmosphere.

The transition of S_2O molecule between electron state is the hotspot of reaserch. Hallin *et al.* first found the excited vibrational state (\tilde{C}^1A'), which has the same symmetry and spin multiplicity with ground state. In the late 1980's, Clouthier and Rutherford measured the vibrational spectrum of this excited state \tilde{C}^1A' and gave detailed explanation. Fueno and Bunker studied the vertical transition energy theoretically and predicted that there exist at least two kinds of molecular configuration with C_{2v} group [2]. Since 1990's, Zhang and Müller mensurated the vibrational level of S_2O again on the basis of the former with the advanced technology [3, 4]. Dudley and Hoffmann studied the potential energy surfaces of ground state and two single excited states using the new developed Perturbation Theory (GVVPT2) [4]. In this work the vibrational spectroscopy of excited state (\tilde{C}^1A') from the known spec-

tra data were calculated. The Hamiltonian were expand into the sum of Casimir operators and Majorana operators [5, 6], then the vibrational levels and the potential energy surface were obtained using algebraic method.

II. BASIC THEORY

For a triatomic molecule, there are two bonds r_1, r_2 , which are related to the group $U(4)$, respectively [7]. So the symmetric group of a triatomic molecule is

$$G = U_1(4) \otimes U_2(4) \quad (1)$$

Hence, the dynamical symmetric subgroup chain can be written as follows:

$$\begin{aligned} U_1(4) \otimes U_2(4) &\supset \left\{ \begin{array}{c} O_1(4) \otimes O_2(4) \\ U_{12}(4) \end{array} \right\} \\ &\supset O_{12}(4) \supset O_{12}(3) \supset O_{12}(2) \end{aligned} \quad (2)$$

where $O_{12}(n) = O_1(n) \oplus O_2(n)$ ($n=2,3,4$). In the work, only the molecular vibrational spectra are considered, so $O_{12}(3)$ and $O_{12}(2)$ can be dropped. The local basis is characterized by:

$$|[N_1][N_2](w_1, 0)(w_2, 0)(\tau_1, \tau_2)\rangle \quad (3)$$

where $[N_i]$ ($i=1,2$) labels the total symmetric representation of $U_i(4)$; $(\omega_i, 0)$ ($i=1,2$) labels the symmetric representation of $O_i(4)$; (τ_1, τ_2) denotes the irreducible representation of $O_{12}(4)$. From the knowledge of Lie algebraic, the Hamiltonian of a triatomic molecule can be written as:

$$\begin{aligned} H = &A_1C_1 + A_2C_2 + A_{12}C_{12} + \lambda M_{12} \\ &+ x_1C_1^2 + x_2C_2^2 + x_3C_1M_{12} + x_4C_2M_{12} \\ &+ x_5C_1^2M_{12} + x_6C_2^2M_{12} + x_7C_1C_{12}M_{12} \\ &+ x_8C_{12}M_{12} + x_9C_1C_2 \dots \end{aligned} \quad (4)$$

C_i, C_i^2 ($i=1,2$), C_{12} are Casimir operators, M_{12} is Majorana operator, $A_1, A_2, A_{12}, \lambda$ are the expansion coefficients, which can be obtained by fitting spectroscopic data. The elements of C_i, C_i^2 ($i=1,2$), C_{12} are diagonal with basis(2), but the elements of M_{12} is non-diagonal.

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The calculation formula is as [8]. For convenience to fit experimental spectrum data, converting the algebraic quantum numbers to the conventional quantum numbers is necessary:

$$\begin{aligned} w_1 &= N_1 - 2v_a \\ w_2 &= N_2 - 2v_c \\ \tau_1 &= N_{12} - 2v - k \\ \tau_2 &= k \\ N_{12} &= N_1 + N_2 \\ v &= v_a + v_b + v_c \end{aligned} \quad (5)$$

Here v_a and v_c are the two stretch vibrational quantum numbers, v_b is the bent vibration quantum number, k has the usual meaning [9]. We can get:

$$\begin{aligned} E(v_a, v_b, v_c, k) &= -4A_1v_a(N_1 + 1 - v_a) \\ &\quad -4A_2v_b(N_2 + 1 - v_b) \\ &\quad -4A_{12}(v_a + v_b + v_c) \\ &\quad \times (N_1 + N_2 - v_a - v_b - v_c) \\ &\quad + \dots \end{aligned} \quad (6)$$

In order to calculate the vibrational levels, the better algebraic Hamiltonian should be got. The value of N_i must be obtained [9]

$$N_i + 2 = \frac{1}{x_{ie}} = \frac{w_{ie}}{w_{ie}x_{ie}} \quad (7)$$

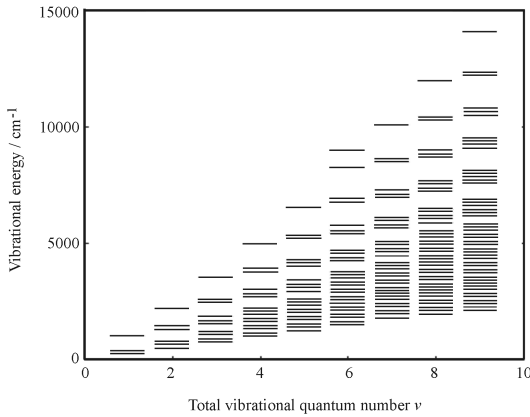


FIG. 1 The diagram of vibrational levels in \tilde{C}^1A' state of S_2O

III. CALCULATIONS OF THE POTENTIAL ENERGY SURFACE

The classical Hamiltonian as the expectation value of H in the coherent state can be obtained. The potential energy surface is defined as

$$V(\mathbf{q}_1, \mathbf{q}_2) = H_{cl}(\mathbf{q}_1, \mathbf{p}_1 = \mathbf{0}; \mathbf{q}_2, \mathbf{p}_2 = \mathbf{0}) \quad (8)$$

where $\mathbf{p}_1, \mathbf{p}_2; \mathbf{q}_1, \mathbf{q}_2$ are the canonical coordinates and momentum, respectively,

$$q_i^2 = e^{-\beta_i(r_i - r_{ie})} \quad (9)$$

$$\frac{\bar{a}_1}{a_2} = \frac{1}{\cosh \alpha(\varphi - \varphi_0)} \quad (10)$$

TABLE I The fitting parameters of S_2O

N_1	182
N_2	264
A_1/cm^{-1}	-1.3165461
A_2/cm^{-1}	-0.38821606
A_{12}/cm^{-1}	-0.12950318
$\lambda_{12}/\text{cm}^{-1}$	$0.26333958 \times 10^{-4}$
x_1/cm^{-1}	$0.14624272 \times 10^{-3}$
x_2/cm^{-1}	$-0.55438813 \times 10^{-6}$
x_7/cm^{-1}	$0.87356277 \times 10^{-10}$
x_8/cm^{-1}	$0.33053798 \times 10^{-6}$
x_9/cm^{-1}	$-0.85205168 \times 10^{-4}$
rms/ cm^{-1}	2.40

\vec{a}_1, \vec{a}_2 are the unit vector along vector $\mathbf{q}_1, \mathbf{q}_2$. φ is the bond angle and φ_0 is the equilibrium bond angle. r_i is the i -th bond length and r_{i0} is the equilibrium bond length. α, β are the spectra parameters, which definition are given out in Ref. [8]. So we can get the potential energy surface with the bond length and bond angle:

$$\begin{aligned} V(r_1, r_2, \phi) &= (A_1 + A_{12})N_1^2[2 - e^{-\beta_1(r_1 - r_{1e})}] \\ &\quad \times e^{-\beta_1(r_1 - r_{1e})} + (A_2 + A_{12})N_2^2 \\ &\quad [2 - e^{-\beta_2(r_2 - r_{2e})}]e^{-\beta_2(r_2 - r_{2e})} + 2A_{12}N_1N_2 \\ &\quad \times \{[2 - e^{-\beta_1(r_1 - r_{1e})}]e^{-\beta_1(r_1 - r_{1e})} \\ &\quad [2 - e^{-\beta_2(r_2 - r_{2e})}]e^{-\beta_2(r_2 - r_{2e})}\}^{1/2} \frac{1}{\cosh \alpha(\phi - \phi_0)} \\ &\quad + \frac{1}{4}\lambda N_1N_2\{2e^{-\beta_1(r_1 - r_{1e})} + 2e^{-\beta_2(r_2 - r_{2e})} \\ &\quad - 2e^{-\beta_1(r_1 - r_{1e}) - \beta_2(r_2 - r_{2e})} \frac{1}{\cosh^2 \alpha(\phi - \phi_0)} \\ &\quad - 2[(2 - e^{-\beta_1(r_1 - r_{1e})})e^{-\beta_1(r_1 - r_{1e})} \\ &\quad \times (2 - e^{-\beta_2(r_2 - r_{2e})})e^{-\beta_2(r_2 - r_{2e})}]^{1/2} \\ &\quad \times \frac{1}{\cosh \alpha(\phi - \phi_0)}\} \end{aligned} \quad (11)$$

IV. RESULTS AND DISCUSSION

With the above theory, the 26 spectrum data of S_2O in excited states \tilde{C}^1A' were fitted with 9 parameters [3]. The values of N_1, N_2 are 182 and 264. The fitting rms and the parameters are listed in Table I. Table II shows the comparison of our results with experimental values. With algebraic method we predict the spectrum data and its labels of quantum number which have not been found in present experiments. We listed all the vibrational level from $v=0$ to $v=9$, which is shown in Fig.1. We also use the potential energy functions to calculate the dissociation energy and force constants. They are listed in Table III.

We got the exact results of vibrational energy with a few parameters, also we got the analytical potential energy surface. With what we have got we can discuss some other characteristics, such as spectrum property, isotopic effect ect.

TABLE II Vibrational energies (in cm⁻¹) in \tilde{C}^1A' state of S₂O(Continued)

$v_1, v_2, v_3,$	Cal.	Exp. [3]	$v_1, v_2, v_3,$	Cal.	Exp. [3]	$v_1, v_2, v_3,$	Cal.	Exp. [3]
0 0 1	255.1	253.78	3 0 3	4240.5		3 3 2	5150.3	
0 1 0	409.2	410.56	3 1 2	4391.2		3 4 1	5293.5	
1 0 0	1036.2	1033.88	3 2 1	4538.8		3 5 0	5433.6	
0 0 2	507.5	506.0	3 3 0	4683.4		4 0 4	5902.5	
0 1 1	663.4	661.98	4 0 2	5445.2		4 1 3	6051.0	
0 2 0	815.4	817.33	4 1 1	5592.9		4 2 2	6196.8	
1 0 1	1285.7	1285.6	4 2 0	5737.8		4 3 1	6339.9	
1 1 0	1438.3	1438.02	5 0 1	6785.8		4 4 0	6480.3	
2 0 0	2215.6		5 1 0	6931.0		5 0 3	7236.7	
0 0 3	756.8	758.3	6 0 0	8257.7		5 1 2	7382.2	
0 1 2	914.5	912.5	0 0 7	1723.5		5 2 1	7525.2	
0 2 1	1068.3	1066.90	0 1 6	6785.8		5 3 0	7665.9	
0 3 0	1218.1	1220.23	0 2 5	2048.7		6 0 2	8701.3	
1 0 2	1532.8	1536.2	0 3 4	2205.5		6 1 1	8844.2	
1 1 1	1686.5	1686.3	0 4 3	2358.4		6 2 0	8985.1	
1 2 0	1836.8	1837.4	1 0 6	2492.6		7 0 1	10291.7	
2 0 1	2459.3		0 5 2	2507.5		7 1 0	10432.8	
2 1 0	2610.1		1 1 5	2652.8		8 0 0	12003.8	
3 0 0	3532.5		0 6 1	2652.8	2652.9	0 0 9	2189.4	
0 0 4	1003.0	1006.1	0 7 0	2794.3	2800.4	0 1 8	2357.0	
0 1 3	1162.5	1161.3	1 2 4	2808.2		0 2 7	2520.9	
0 2 2	1318.0	1315.2	1 3 3	2960.6		0 3 6	2680.9	
0 3 1	1469.6	1468.43	1 4 2	3109.5		0 4 5	2837.2	
0 4 0	1617.3	1618.92	1 5 1	3254.8		1 0 8	2957.1	
1 0 3	1776.5		1 6 0	3396.5		0 5 4	2989.7	
1 1 2	1935.0	1938.3	2 0 5	3410.5		1 1 7	3119.3	
1 2 1	2083.8		2 1 4	3565.7		0 6 3	3138.4	
1 3 0	2231.9	2229.5	2 2 3	3717.6		1 2 6	3278.0	
2 0 2	2700.5		2 3 2	3866.3		0 7 2	3283.3	
2 1 1	2852.5		2 4 1	4011.6		0 8 1	3424.5	3428.0
2 2 0	3001.1		2 5 0	4153.6		1 3 5	3433.1	
3 0 1	3770.5		3 0 4	4472.7		0 9 0	3562.0	3565.1
3 1 0	3919.6		3 1 3	4624.1		1 4 4	3584.7	
4 0 0	4981.9		3 2 2	4772.4		1 5 3	3732.8	
0 0 5	1246.1		3 3 1	4917.8		2 0 7	3872.6	
0 1 4	1407.3	1408.3	3 4 0	5060.2		1 6 2	3877.4	
0 2 3	1546.6		4 0 3	5674.6		1 7 1	4018.5	
0 3 2	1718.0		4 1 2	5822.7		2 1 6	4029.9	
0 4 1	1867.5	1866.8	4 2 1	5968.1		1 8 0	4156.1	
0 5 0	2013.0	2012.44	4 3 0	6110.8		2 2 5	4183.9	
1 0 4	2017.8		5 0 2	7011.8		2 3 4	4334.6	
1 1 3	2174.7		5 1 1	7157.2		2 4 3	4482.1	
1 2 2	2327.9		5 2 0	7300.1		2 5 2	4626.3	
1 3 1	2477.5		6 0 1	8479.9		2 6 1	4767.3	
1 4 0	2623.5		6 1 0	8623.1		2 7 0	4905.2	
2 0 3	2939.5		7 0 0	10074.4		3 0 6	4931.4	
2 1 2	3092.6		0 0 8	1957.9		3 1 5	5084.2	
2 2 1	3242.3		0 1 7	2124.0		3 2 4	5234.1	
2 3 0	3388.7		0 2 6	2286.2		3 3 3	5380.9	
3 0 2	4006.5		0 3 5	2444.7		3 4 2	5524.8	
3 1 1	4156.3		0 4 4	2599.3		3 5 1	5665.8	

Table II continued

$v_1, v_2, v_3,$	Cal	Exp. [3]	$v_1, v_2, v_3,$	Cal	Exp. [3]	$v_1, v_2, v_3,$	Cal.	Exp. [3]
3 2 0	4303.2		1 0 7	2726.1		3 6 0	5803.8	
4 0 1	5214.3		0 5 3	2750.1		4 0 5	6128.8	
4 1 0	5361.5		1 1 6	2887.0		4 1 4	6277.7	
5 0 0	6558.6		0 6 2	2897.1		4 2 3	6424.0	
0 0 6	1486.3		0 7 1	3040.3	3044.9	4 3 2	6567.5	
0 1 5	1649.2		1 2 5	3044.4		4 4 1	6708.4	
0 2 4	1808.2		0 8 0	3179.8	3182.8	4 5 0	6846.6	
0 3 3	1963.3		1 3 4	3195.2		5 0 4	7460.4	
0 4 2	2114.5		1 4 3	3348.4		5 1 3	7606.0	
1 0 5	2256.5		1 5 2	3495.1		5 2 2	7749.2	
0 5 1	2261.8		1 6 1	3638.3		5 3 1	7889.9	
0 6 0	2405.3	2405.3	2 0 6	3642.6		5 4 0	8028.3	
1 1 4	2414.8		1 7 0	3778.0		6 0 3	8921.8	
1 2 3	2569.4		2 1 5	3798.9		6 1 2	9064.6	
1 3 2	2720.4		2 2 4	3951.9		6 2 1	9205.2	
1 4 1	2867.9		2 3 3	4101.6		6 3 0	9343.8	
1 5 0	3011.7		2 4 2	4248.0		7 0 2	10508.6	
2 0 4	3176.1		2 5 1	4391.1		7 1 1	10649.1	
2 1 3	3330.3		2 6 0	4531.1		7 2 0	10787.8	
2 2 2	3481.1		3 0 5	4702.9		8 0 1	12216.5	
2 3 1	3628.7		3 1 4	4855.1		8 1 0	12355.3	
2 4 0	3772.9		3 2 3	5004.2		9 0 0	14041.2	

TABLE III The dissociation energy and force constant of S₂O

	This work	Ref.[11]
$K_{11}/(\text{aJ}^2/\text{\AA}^2)$	6.3854	6.80068
$K_{12}/(\text{aJ}^2/\text{\AA}^2)$	935.008×10^{-7}	
$K_{33}/(\text{aJ}^2/\text{\AA}^2)$	1.2013	
De/eV	18.02346	
De_1/eV	7.3102	
De_2/eV	4.8216	

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[1] P. W. Schenk and Z. Anorg. Allg. Chem. **211**, 150 (1933).

- [2] F. Takayuki and J. Robert, *Theor. Chim. Acta.* **73**, 123 (1988).
- [3] Q. Zhang, P. Dupr e, B. Grzybowski, *et al.* *J. Chem. Phys.* **103**, 67 (1995).
- [4] T. M uller and P. H. Vaccaro, *J. Chem. Phys.* **15**, 5038 (1999).
- [5] F. Iachello and R. D. Levine, *Algebraic Theory of Molecules*, Oxford: Oxford University, 1994. 90
- [6] B. G. Wybourne, Translated by Feng Cheng-Tian. *Classical Groups and Their Application in Physics*, Beijing: Science Press, 295 (1982).
- [7] F. Iachello and R. D. Levine, *J. Chem. Phys.* **77**, 3046 (1982).
- [8] Y. J. Zheng and S. L. Ding, *Science in China (Series B)*, **30**, 183 (2000).
- [9] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules*, New York: Van Nostrand, 230 (1950).
- [10] O. S. Van Roosmalen, F. Iachello, R. D. Levine, *et al.* *J. Chem. Phys.* **79**, 2525 (1983).
- [11] H. X. Han, Q. Peng, Z. Y. Wen, *et al.* *Sci. J. Northwest University* **2**, 7 (2004).