

# TRUE POTENTIAL ENERGY CURVES AND DISSOCIATION ENERGIES OF SiF AND GeF MOLECULES

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## ABSTRACT

The true experimental potential energy curves have been constructed for the different electronic states of astrophysically important molecule SiF and GeF molecules, by the method of Lakshman and Rao along with Jarmain method. The ground state dissociation energies for these two molecules have been estimated by curve fitting method using the H-H function. From these studies, it is concluded that the ionization potential of silicon is greater than that of silicon fluoride molecule.

## INTRODUCTION

THE construction of potential energy curves is of considerable importance for the understanding of physical problems arising in astrophysics, gas kinetics and molecular spectra. Silicon monofluoride is of astrophysically interest and may be a constituent of the Sun<sup>1</sup>. The rotational structure of the  $\gamma$  bands of SiF molecule has been completely analysed by Appelblad *et al.*<sup>2</sup> and Martin and Merer<sup>3</sup> reexamined the a  $^4\Sigma^- - X^2\Pi$  transition. Singh and Rai<sup>4</sup> have computed a potential energy curve for the ground state of SiF molecule. The UV band system and emission spectra of GeF, SiF, SnF and PbF were observed by Barrow *et al.*<sup>5,6</sup>. Recently Martin and Merer<sup>7,8</sup> carried out rotational structure analysis of GeF molecule. The rotational and vibrational

constants required for the present work have been taken from Mizushima<sup>9</sup> and Martin and Merer<sup>7,8</sup>. The present paper deals with the construction of potential energy curves by the methods of Lakshman and Rao<sup>11</sup> along with Jarmain<sup>10</sup>.

## RESULTS AND DISCUSSION

The true potential energy curves have been drawn for eight states of SiF and ten different states of GeF molecules using these two methods. The authors' method<sup>10</sup> was successfully verified in a number of cases<sup>12-14</sup>. The agreement between these two methods is excellent. For brevity, only alternate turning points for different electronic states of SiF and GeF molecules are presented in Table I. The maximum deviation between the two values is less than 3%.

TABLE I

*The true potential energy curves for different electronic states of SiF and GeF molecules*

$v$	U + Te (cm <sup>-1</sup> )	Authors' method		Jarmain method	
		$r_{\min}$ (Å)	$r_{\max}$ (Å)	$r_{\min}$ (Å)	$r_{\max}$ (Å)
SiF molecule					
Te = 0					
0	427.41	1.544	1.663	1.545	1.663
2	2113.37	1.484	1.750	1.484	1.751
4	3761.41	1.450	1.812	1.451	1.812
6	5371.53	1.426	1.864	1.426	1.865
8	6943.73	1.406	1.913	1.406	1.913
Tc = 22787.64					
A <sup>2</sup> Σ <sup>+</sup> state					
0	23215.05	1.555	1.673	1.555	1.674
2	24901.01	1.495	1.761	1.495	1.760
4	26549.05	1.461	1.823	1.461	1.823
6	28159.17	1.437	1.875	1.437	1.875
8	29731.37	1.418	1.924	1.418	1.924

TABLE I (Contd.)

$v$	$U + Te$ (cm <sup>-1</sup> )	Authors' method		Jarman method	
		$r_{min}$ (Å)	$r_{max}$ (Å)	$r_{min}$ (Å)	$r_{max}$ (Å)
Te = 29808.41		$a^4\Sigma^-$ state			
0	30238.65	1.548	1.666	1.549	1.666
1	31091.07	1.512	1.717	1.512	1.717
3	32763.69	1.470	1.787	1.470	1.787
5	34393.35	1.442	1.843	1.442	1.843
Te = 34561.50		B $^2\Sigma^+$ state			
0	35065.91	1.489	1.598	1.489	1.598
2	37109.42	1.432	1.679	1.433	1.678
4	39014.33	1.401	1.733	1.401	1.733
6	40930.64	1.378	1.780	1.378	1.780
8	42808.35	1.359	1.823	1.359	1.823
10	44647.46	1.344	1.863	1.344	1.863
Te = 39537.45		C $^2\Delta$ state			
0	39981.90	1.516	1.632	1.517	1.632
1	40860.29	1.480	1.682	1.480	1.682
2	41724.66	1.457	1.720	1.457	1.720
Te = 41964.90		C' $^2\Pi$ state			
0	42479.69	1.477	1.584	1.477	1.585
2	44516.59	1.419	1.662	1.420	1.662
4	46517.88	1.387	1.715	1.387	1.715
6	48483.58	1.363	1.760	1.363	1.760
Te = 46606.70		D' $^2\Pi$ state			
0	47121.83	1.483	1.596	1.488	1.596
1	48144.17	1.450	1.635	1.454	1.642
2	49153.95	1.426	1.669	1.430	1.673
Te = 47418.60		D $^2\Sigma^+$ state			
0	47918.79	1.492	1.601	1.489	1.598
1	48910.71	1.458	1.648	1.455	1.644
3	50860.71	1.420	1.713	1.417	1.713
GeF molecule					
Te = 0		X $^2\Pi_{1/2}$ state			
0	332.05	1.694	1.806	1.691	1.807
2	1644.99	1.633	1.895	1.631	1.892
4	2932.35	1.600	1.954	1.598	1.951
6	4195.63	1.575	2.004	1.573	2.001

TABLE I (Contd.)

$v$	U + Te (cm <sup>-1</sup> )	Authors' method		Jarmain method	
		$r_{\min}$ (Å)	$r_{\max}$ (Å)	$r_{\min}$ (Å)	$r_{\max}$ (Å)
Te = 934.33		X $^2\Pi_{3/2}$ state			
0	1267.21	1.692	1.808	1.689	1.805
2	2582.97	1.626	1.895	1.629	1.890
4	3874.15	1.598	1.952	1.596	1.949
6	5138.69	1.573	2.002	1.571	1.999
8	6387.40	1.554	2.048	1.551	2.045
Te = 23316.65		A $^2\Sigma^+$ state			
0	23522.18	1.799	1.947	1.797	1.945
2	24342.00	1.725	2.056	1.722	2.053
4	25151.35	1.685	2.132	1.683	2.128
6	25950.31	1.657	2.196	1.654	2.193
8	26738.27	1.635	2.255	1.632	2.252
10	27514.61	1.617	2.311	1.614	2.307
Te = 35010.85		B $^2\Sigma^-$ state			
0	35408.44	1.620	1.724	1.621	1.722
2	36980.93	1.577	1.817	1.575	1.814
4	38525.28	1.547	1.871	1.544	1.867
6	40042.04	1.527	1.915	1.522	1.912
8	41531.84	1.505	1.956	1.503	1.953
10	42995.26	1.489	1.994	1.487	1.992
Te = 35194.68		$a$ $^4\Sigma^-$ state			
0	35513.83	1.691	1.810	1.688	1.808
2	36757.13	1.621	1.910	1.619	1.907
4	37947.15	1.598	1.967	1.595	1.964
Te = 43369.61		C' $^2\pi$ state			
0	43767.19	1.623	1.729	1.620	1.727
2	45359.67	1.561	1.805	1.563	1.802
4	46948.65	1.533	1.859	1.532	1.854
6	48534.90	1.508	1.905	1.507	1.899
Te = 43977.49		C $^2\Delta$ state			
0	44326.47	1.646	1.760	1.643	1.756
1	45010.48	1.612	1.810	1.609	1.808
2	45675.87	1.591	1.851	1.588	1.848
Te = 46645.41		E $^2\Sigma^+$ state			
0	47024.70	1.624	1.732	1.621	1.730
2	48527.06	1.565	1.810	1.563	1.807
4	50005.69	1.532	1.863	1.530	1.860
Te = 47920.73		D' $^2\Pi$ state			
0	48321.86	1.620	1.726	1.618	1.723
1	49119.06	1.586	1.770	1.584	1.767
Te = 49412.89		G $^2\Delta$ state			
0	49770.19	1.653	1.765	1.651	1.762
2	51185.29	1.588	1.841	1.590	1.842
3	51884.38	1.574	1.873	1.572	1.871

The true potential energy curves have been used to estimate the dissociation energies of diatomic molecules in a number of cases by fitting an empirical potential energy curve. The Hulburt-Hirschfelder function<sup>15</sup> has been shown to fit to a good extent to the true potential energy curves. Using H-H function the dissociation energy  $D_0$ , in the ground state of SiF molecule, is estimated to be 4.846 eV, which is in good agreement with the values given by Gaydon<sup>16</sup> ( $5.0 \pm 0.5$  eV) and Herzberg<sup>17</sup> (4.80 eV). Following the same procedure the  $D_0$  value, for the ground state of GeF molecule has been evaluated as 4.422 eV, which is comparable with the values suggested by Gaydon<sup>16</sup> ( $5.0 \pm 1.0$  eV) and Herzberg<sup>17</sup> (4.90 eV).

The values cited in the literature for the ionization potential of SiF are quite harmonious. Keeping this aim in mind, the authors took up the calculations of the ionization potential of SiF and GeF molecules. O'Hare and Wahl.<sup>1</sup> have shown the difference between SiF<sup>+</sup> and SiF bond energies by the relation

$D_0(\text{SiF}^+) - D_0(\text{SiF}) = I(\text{Si}) - I(\text{SiF})$  is  $0.8 \pm 0.3$  eV, which is consistent with the ionization of a antibonding electron. It expresses that SiF<sup>+</sup> has one antibonding electron fewer than SiF and so one would expect  $D_0(\text{SiF}^+)$  to be larger than  $D_0(\text{SiF})$ .

Having known the  $D_0$  values of SiF, GeF, the ionization potentials for these molecules are calculated assuming ionization potentials of silicon, germanium and  $D_0$  values of SiF<sup>+</sup>, GeF<sup>+</sup> from Gaydon<sup>16</sup>

$$\begin{aligned} I(\text{SiF}) &= I(\text{Si}) + D_0(\text{SiF}) - D_0(\text{SiF}^+) \\ &= 8.15 + 4.85 - 5.90 \\ &= 7.10 \text{ eV.} \end{aligned}$$

The ionization potential 7.10 eV for SiF is in excellent agreement with the value of  $7.4 \pm 0.2$  eV proposed by O'Hare and Wahl.<sup>1</sup> Similarly the ionization potential of GeF is estimated as 6.70 eV which is in close agreement with the value 7.2 eV proposed by Harland *et al.*<sup>18</sup> and 7.46 eV given by Martin and McCrei<sup>8</sup>.

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- O'Hare, P. A. G. and Wahl. Arnold, C., *J. Chem. Phys.*, 1971, **55**, 666.
- Appelblad, O., Barrow, R. F. and Veima, R. D., *J. Phys. B. (Proc. Phys. Soc.)*, 1968, **1**, 274.
- Martin, R. W. and Merer, A. J., *Can. J. Phys.*, 1973, **51**, 634.
- Singh, R. B. and Rai, D. K., *Ind. J. Pure and Appl. Phys.*, 1966, **4**, 102.
- Barrow, R. F. and Lagerqvist, A., *Ark. Phys.*, 1949, **1**, 221.
- , Butler, D., Johns, J. W. C. and Powell, J. L., *Proc. Phys. Soc.*, 1959, **73**, 317.
- Martin, R. W. and Merer, A. J., *Can. J. Phys.*, 1973, **51**, 125.
- and —, *Ibid.*, 1974, **52**, 1458.
- Mizushima, Masataka, *Rotating Diatomic Molecules*, John Wiley and Sons, New York, 1975.
- Lakshman, S. V. J. and Ramakrishna Rao, T. V., *Jol. Phys., B*, 1971, **4**, 269.
- Jarmain, W. R., *Can. J. Phys.*, 1960, **38**, 217.
- Ramakrishna Rao, T. V. and Lakshman, S. V. J., *Physica*, 1971, **56**, 332.
- and —, *Jol. Quant. Spectro. Radi. Trans.*, 1972, **12**, 1063.
- Lakshman, S. V. J., Ramakrishna Rao, T. V. and Naidu, G. T., *Curr. Sci.*, 1978, **47**, 7.
- Hulburt, H. H. and Hirschfelder, J. O., *J. Chem. Phys.*, 1941, **9**, 61; *Ibid.*, 1961, **35**, 1901.
- Gaydon, A. G., *Dissociation Energies*, Chapman and Hall, Ltd., London, 1968.
- Herzberg, G., *Mol. Spectra and Mol. Structure, I*, Van, Nostrand Company, New York, 1967.
- Harland, P. W., Craddock, S. and Thynne, J. C. J., *Inorg. Nucle. Chem. Lett.*, 1973, **9**, 53.

## CONFERENCE ON ALUMINIUM METALLURGY RESEARCH, DEVELOPMENTS AND TECHNOLOGY

The Metallurgical Society and The Department of Metallurgy, Indian Institute of Science, Bangalore 560 012, have organized a Conference on the above subject during September 1979. The Conference deals with a variety of topics connected with aluminium extraction, physical metallurgy, corrosion, powder

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