

THE TRUE POTENTIAL ENERGY CURVES AND DISSOCIATION ENERGY OF TITANIUM MONOXIDE

S. V. J. LAKSHMAN*, T. V. RAMAKRISHNA RAO AND G. T. NAIDU
Department of Physics, SVU Post-Graduate Centre, Anantapur 515 003, India

ABSTRACT

The true potential energy curves have been constructed for the different electronic states of astrophysically important molecule TiO by the method of Lakshman and Rao². The dissociation energy for the ground state of the above molecule has been estimated by fitting the H-H function to the true potential energy curves. The dissociation energy thus obtained is in good agreement with the values reported in literature.

INTRODUCTION

THE construction of accurate potential energy curves is of considerable importance for the understanding of physical problems arising in astrophysics, gas kinetics and molecular spectra. Since the molecule is of astrophysical importance whose spectra were observed in the sunspots, M and S types of stars¹, authors took up the present work. The present paper deals with the construction of experimental potential energy curves and dissociation energy of TiO for which sufficient spectroscopic data are available.

METHOD OF COMPUTATION

The present method of Lakshman and Rao² was successfully verified by them in number of cases²⁻⁷ and recently Chakraborty and Pan⁸ in their review paper gave a detailed account of different methods and the authors' method is one such reliable and accurate, which involves less complicated mathematical calculations. Since the details of this method are reported in literature², only the explicit formulae to evaluate the turning points are given below :

$$f = \left(\frac{8\pi^2 \mu c (\omega x)_i}{h} \right)^{-1/2} 1/W_i$$

$$g = \left(\frac{2\pi^2 \mu c}{h} \right)^{1/2} \{ 2a_i (\omega x)_i^{-1} U_i^{1/2} + (\omega x)_i^{-1/2} [2B_i - a_i \omega_i (\omega x)_i^{-1}] \ln W_i \}$$

where

$$W_i = \frac{[\omega_i^2 - 4(\omega x)_i U_i]^{1/2}}{\omega_i - 2(\omega x)_i^{1/2} U_i^{1/2}}$$

the symbols have their usual spectroscopic significance. The classical turning points are given by the relation

$$r_{\max, \min} = (f/g + f^2)^{1/2} \pm f.$$

RESULTS AND DISCUSSION

The experimental potential energy curves for three states X ³Δ, A ³Σ, C ³Δ, of TiO molecule have been constructed by Kushawaha⁹ based on the molecular constants given by Uhler¹⁰. In the present study using more accurate and reliable vibrational and rotational constants the turning points for the B ³π, a ¹Δ, d ¹Σ⁺, b ¹π, c ¹Φ, e ¹Σ along with X ³Δ states of TiO molecule have been calculated to draw the experimental true potential energy curves. For the triplet states the rotational and vibrational constants have been taken from Collins¹¹ and for singlet states the vibrational and rotational constants were taken from Phillips¹²⁻¹⁴, Pettersson¹⁵⁻¹⁶, Linton *et al.*¹⁷, Phillips *et al.*¹⁸, Lindgren¹⁹, Linton *et al.*²⁰, Linton²¹, and summarised in Table I.

TABLE I
Spectroscopic constants of TiO molecule

State	T _e (cm ⁻¹)	ω _e (cm ⁻¹)	ω _e x _e (cm ⁻¹)	β (cm ⁻¹)	α _e (cm ⁻¹)	r _e (Å)
<i>TiO Molecule</i>						
X ³ Δ	0	1009.0208	4.4978	0.535412	0.003011	1.6201
B ³ π	16214.0	871.96	4.1135	0.507812	0.0032758	1.6635
a ¹ Δ	581.0	1016.3	3.93	0.53760	0.00298	1.6167
d ¹ Σ ⁺	1708.0	1023.8	4.64	0.5490	0.00337	1.6000
b ¹ π	10814.0	918.7	3.75	0.51329	0.00290	1.6540
c ¹ Φ	18471.5	916.7	4.33	0.52301	0.00313	1.6391
e ¹ Σ	26005.8	853.9	4.7	0.4892	0.0025	1.6950

* Department of Physics, S.V. University, Tirupati.

Employing the method of Lakshman and Rao², the turning points for different vibrational levels of $X^3\Delta$, $B^3\pi$, $a^1\Delta$, $d^1\Sigma^+$, $b^1\pi$, $c^1\Phi$ and $e^1\Sigma$ states of TiO molecule have been calculated and presented in Table II. The extrapolated energy values for the highest bound level v , and the corresponding turning points are evaluated and included in this table at the end of observed levels in each state.

TABLE II

The true potential energy curves for different states of TiO Molecule

v	$U(\text{cm}^{-1})$	$U + \text{Te}$ (cm^{-1})	$r_{\min}(\text{\AA})$	$r_{\max}(\text{\AA})$
$X^3\Delta$ state				
$\text{Te} = 0$				
0	503.4	503.4	1.569	1.675
1	1503.4	1503.4	1.535	1.719
2	2494.4	2494.4	1.513	1.751
3	3476.5	3476.5	1.495	1.778
4	4449.5	4449.5	1.480	1.802
5	5413.6	5413.6	1.468	1.825
6	6368.6	6368.6	1.456	1.846
7	7314.7	7314.7	1.446	1.867
8	8251.7	8251.7	1.437	1.886
9	9179.8	9179.8	1.428	1.905
10	10098.8	10098.8	1.420	1.923
11	11008.9	11008.9	1.413	1.941
12	11910.0	11910.0	1.406	1.959
13	12802.1	12802.1	1.399	1.976
14	13685.1	13685.1	1.392	1.993
15	14559.2	14559.2	1.386	2.010
16	15424.3	15424.3	1.380	2.027
17	16280.4	16280.4	1.374	2.044
18	17127.5	17127.5	1.369	2.060
19	17965.6	17965.6	1.364	2.076
20	18794.7	18794.7	1.359	2.092
21	19614.8	19614.8	1.354	2.108
111(v_e)	56588.0	56588.0	0.823	6.465
$B^3\pi$ state				
$\text{Te} = 16214.0 \text{ cm}^{-1}$				
0	435.0	16649.0	1.609	1.723
1	1298.7	17512.7	1.572	1.770
2	2154.2	18368.2	1.549	1.805
3	3001.5	19215.5	1.530	1.835
4	3840.5	20054.5	1.515	1.862
5	4671.3	20885.3	1.502	1.886
105(v_e)	46207.5	62421.5	0.815	7.909
$a^1\Delta$ state				
$\text{Te} = 581.0 \text{ cm}^{-1}$				
0	507.2	1088.2	1.566	1.671
1	1515.6	2096.6	1.532	1.715
2	2516.2	3097.2	1.510	1.747
3	3508.9	4089.9	1.492	1.774
4	4493.8	5074.8	1.478	1.798
5	5470.8	6051.8	1.465	1.820
129(v_e)	65703.8	66284.8	0.736	9.247
$d^1\Sigma^+$ state				
$\text{Te} = 1708.0 \text{ cm}^{-1}$				
0	510.7	2218.7	1.549	1.654
1	1525.3	3233.3	1.516	1.698
2	2530.5	4238.5	1.494	1.730
3	3526.5	5234.5	1.477	1.758
4	4513.1	6221.1	1.462	1.782
5	5490.5	7198.5	1.447	1.800
6	6458.7	8166.7	1.439	1.826
7	7417.5	9125.5	1.429	1.847
110(v_e)	56474.3	58182.3	0.717	8.535
$b^1\pi$ state				
$\text{Te} = 10814.4 \text{ cm}^{-1}$				
0	458.4	11272.0	1.601	1.712
1	1369.6	12184.0	1.565	1.758
2	2273.3	13087.7	1.542	1.791
3	3169.4	13983.8	1.524	1.820
4	4058.0	14872.4	1.508	1.845
5	4939.1	15753.5	1.495	1.869
122(v_e)	56267.3	67081.7	0.666	10.406
$c^1\Phi$ state				
$\text{Te} = 18471.5 \text{ cm}^{-1}$				
0	457.3	18928.8	1.586	1.697
1	1365.3	19836.8	1.550	1.743
2	2264.8	20736.3	1.527	1.777
3	3155.5	21627.0	1.508	1.805
105(v_e)	48517.9	66989.4	0.721	7.992
$e^1\Sigma$ state				
$\text{Te} = 26005.8 \text{ cm}^{-1}$				
0	425.8	26431.6	1.639	1.754
1	1270.3	27276.1	1.602	1.802
2	2105.4	28111.2	1.577	1.836
3	2931.1	28936.9	1.557	1.866
4	3747.4	29753.2	1.541	1.892
5	4554.3	30560.1	1.526	1.917
6	5351.8	31357.6	1.513	1.940
90(v_e)	38783.8	64789.6	0.347	7.216

The true potential energy curves (RKR) have been used to estimate the dissociation energies of diatomic molecules in a number of cases by fitting an empirical potential energy curve²²⁻²⁵. The Hulburt-Hirschfelder function has been shown to fit to a good extent the RKR curves wherever these are known over a wide range of energy for a number of diatomic molecules (Steele *et al.*²²).

Hulburt-Hirschfelder function²⁶,

$$U = D_e [(1 - e^{-x})^2 + cx^3 e^{-2x} (1 + bx)]$$

where

$$x = \frac{\omega_e}{2(B_e D_e)^{1/2}} \frac{r - r_e}{r_e}; \quad c = 1 + a_1 \left(\frac{D_e}{a_0}\right)^{1/2}$$

$$b = 2 - \left(\frac{7}{2} - \frac{D_e a_2}{a_0}\right) / c$$

and a_0, a_1, a_2 are constants given by

$$a_0 = \frac{\omega_e^2}{4B_e}, \quad a_1 = -1 - \frac{\omega_e a_e}{6B_e^2}$$

$$a_2 = \frac{5}{4} a_1^2 - \frac{2\omega_e x_e}{3B_e} \quad \text{and} \quad D_e = \frac{\omega_e^2}{4\omega_e x_e}$$

being five parameter function gives best average results and in general gives the best fit of the potential for all the cases studied whereas Lippincott 3-parameter potential function gives nearly good results. Varshni III and Lippincott functions, the best of the three-parameter functions in fitting the potential energy curves, both give good prediction of dissociation energy values. On the other hand, the Lippincott function gives fairly reliable values of D_e , while Varshni III function does not. According to the study of comparison of potential functions by Steele, Lippincott and Vanderslice²² the better 3-parameter functions give potential curves with an average error of 2 to 3% in $|V - V_{RKR}|/D_e$ whereas the better five-parameter function should give only average error of 1 to 2%.

The most prominent feature of these curves is that these are narrow well type potentials which indicate that the molecule behaves approximately like a harmonic oscillator rather than an anharmonic oscillator as has been observed by Kushawaha⁹. The true potential energy curves are lying approximately one above the other indicating the structure of the molecule in the ground and the upper states should be nearly the same as is evident from the approximately equal r_e values for all these states.

The results of the calculation for the ground state dissociation energy is given in Table III. From this table one can conclude that the best fit to the RKR curve is obtained when we put $D_e = 56,500 \text{ cm}^{-1}$ (7.005 eV). The most probable value of D_e from our calculations is 7.005 eV since $|V - V_{RKR}|/D_e$ is 0.3%. The value obtained by

TABLE III

Calculations for the ground-state dissociation energy of TiO molecule using the H-H function

r (Å)	$D_e = 56,000 \text{ cm}^{-1}$	$D_e = 56,500 \text{ cm}^{-1}$	$D_e = 58,000 \text{ cm}^{-1}$	RKR cm^{-1}
1.675	492.1	496.5	509.7	503.4
1.719	1483.3	1496.6	1536.3	1503.4
1.778	3428.2	3458.8	3550.6	3476.5
1.802	4373.4	4412.5	4529.6	4449.5
1.846	6277.7	6333.7	6501.9	6368.6
1.867	7248.3	7313.0	7507.2	7314.7
1.905	9078.9	9160.1	9403.2	9179.8
1.923	9971.4	10060.4	10327.5	10098.8
1.976	12657.8	12770.8	13109.8	12802.1
1.993	13529.9	13650.7	14013.1	13685.1
2.027	15277.5	15413.9	15823.1	15424.3
2.044	16149.1	16293.3	16725.8	16280.4
2.076	17782.0	17940.8	18417.1	17965.6
1.513	2469.1	2491.2	2557.3	2494.4
1.468	5377.6	5425.6	5569.6	5413.6
1.437	8215.0	8288.4	8508.4	8251.7
1.413	10945.9	11043.7	11336.9	11008.9
1.406	11837.7	11943.4	12260.5	11910.0
1.386	14629.9	14760.5	15388.5	14559.2
1.369	17150.0	17303.1	17947.3	17127.5
1.359	18853.9	19022.3	19732.6	18794.7
1.354	19849.9	20032.9	20667.4	19614.8

Kushawaha⁹ is based on the curve fitting, using the old rotational constants and also the uncertainty of $\pm 20 \text{ K cal/mol}$ (experimental value) for which unconvincing explanation in his article and only the main value included in the text and assumes the uncertainty of the D_e of TiO with that of Wahlbeck's²⁷ uncertainty value, since these two are independent works the uncertainty cannot be the same even though main value be the same.

The dissociation energy of TiO molecule has been given by different authors (Gaydon²⁶, Herzberg²⁸, Drowart *et al.*²⁹, Gilles *et al.*³⁰, and Kushawaha⁹). In the present work using the Hulburt-Hirschfelder function, the dissociation energy for the ground state of TiO molecule is estimated to be 7.005 eV which is in very good agreement with the value given by Gaydon²⁶ (7.2 \pm 0.1 eV).

ACKNOWLEDGEMENTS

The authors are thankful to Prof. S. V. Subrahmanyam for his interest and encouragement in the present work. One of the authors (GTN) wishes to thank U.G.C., New Delhi, for financial assistance.

1. Davis, D. N., *Astrophys. J.*, 1947, 106, 28.
2. Lakshman, S. V. J. and Ramakrishna Rao, T. V., *J. Phys. B*, 1971, 4, 269.
3. Ramakrishna Rao, T. V. and Lakshman, S. V. J., *J. Quant. Spectro. Radiat. Transfer.*, 1972, 12, 1063.
4. — and —, *Physica*, 1971, 56, 322.
5. — and —, *Ind. J. Pure and Appl. Phys.*, 1973, 11, 539.
6. Lakshman, S. V. J., Ramakrishna Rao, T. V. and Naidu, G. T., *Pramāna*, 1976, 7, 369.
7. —, — and —, *Curr. Sci.*, 1977, 46, 33.
8. Chakraborty, B. and Pan, Y. K., *Applied Spectro.*, 1973, 7, 283.
9. Kushawaha, V. S., *J. Phys. Chem.*, 1973, 77, 2885.
10. Uhler, U., *Ph.D. Thesis*, University of Stockholm, Sweden, 1954.
11. Collins, J. G., *J. Phys., B*, 1975, 8, 304.
12. Phillips, J. G., *Astrophys. J.*, 1950, 111, 314.
13. —, *Ibid.*, 1969, 157, 449.
14. —, *Apply. J.*, 1973, 26, 313.
15. Pettersson, A. V., *Ark. Fys.*, 1959, 16, 185.
16. — and Lindgren, B., *Ibid.*, 1962, 22, 491.
17. Linton, C. and Nicholls, R. W., *J. Phys., B*, 1969, 2, 490.
18. Phillips, J. G. and Davis, S. P., *Astrophys. J.*, 1971, 167, 209.
19. Lindgren, B., *J. Mol. Spectro.*, 1972, 43, 474.
20. Linton, C. and Singhal, S. R., *Ibid.*, 1974, 51, 194.
21. —, *Ibid.*, 1974, 50, 235.
22. Steele, D., Lippincott, E. R. and Vanderslice, J. T., *Rev. Mod. Phys.*, 1962, 34, 239.
23. Singh, R. B. and Rai, D. K., *Canad. J. Phys.*, 1965, 43, 829.
24. Singh, J., Nair, K. P. R. and Rai, D. K., *J. Mol. Struct.*, 1970, 5, 492.
25. Nair, K. P. R., Singh, R. B. and Rai, D. K., *J. Chem. Phys.*, 1965, 43, 3570.
26. Gaydon, A. G., *Dissociation Energies*, Chapman and Hall, Ltd. (London), 1968.
27. Wahlbeck, P. G. and Gilles, P. W., *J. Chem. Phys.*, 1967, 46, 2465.
28. Herzberg, G., *Mol. Spectra and Mol. Structure—I*, Van Nostrand Company, New York, 1967.
29. Drowart, J., Coppens, P. and Smoes, S., *J. Chem. Phys.*, 1969, 50, 1046.
30. Gilles, P. W., Hamson, P. J. and Wahlbeck, P. G., *Ibid.*, 1969, 50, 1048.

DETERMINATION OF URANIUM TRACE IN SOME SEMICONDUCTING MATERIALS BY NUCLEAR TRACK DETECTORS

S. K. CHAKARVARTI

Department of Applied Physics, Regional Engineering College, Kurukshetra 132119, Haryana, India

AND

M. M. DHAWAN AND K. K. NAGPAUL

Department of Physics, Kurukshetra University, Kurukshetra 132119, Haryana, India

ABSTRACT

Fission track counting method has been applied to the trace determination of uranium in some semiconductors Se, Te, As₂-S₃ (Glass), CdS, PbS, Pb-As-S and Pb-Sb-S in amorphous form. It has been found that the uranium is not uniformly distributed. Results indicate uranium concentration as low as 0.43 ppm in the homogeneous region and 77 ppm on the higher side in the heterogeneous region.

INTRODUCTION

ONE of the significant applications of solid state nuclear track detectors (SSNTD) lies in determining some trace elements¹ (U²³⁵, B¹⁰, Li⁷, Li⁶, O¹⁷, K³⁹, Fe⁵⁷, S³³, Zn⁶⁶, etc.), in various materials. In the present investigations, attempt has been made to apply this technique to semiconductors for the determination of traces of uranium.

EXPERIMENTAL PROCEDURE

The method consists of placing suitable plastic detectors in close and intimate contact on both sides of the sample under investigation. A standard sample with known uranium content or other isotope of interest is also included. All the samples are then enclosed in an aluminium capsule and the whole assembly irradiated to thermal neutrons of