

# TRUE POTENTIAL ENERGY CURVES, DISSOCIATION ENERGY AND $r$ -CENTROIDS OF DIATOMIC GeO

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FROM the results reported by Murthy *et al.*<sup>1-2</sup> on rotational analysis of some bands of GeO molecule in the region  $\lambda$  2200– $\lambda$  4200 Å, it is found that the transition involved is  ${}^1\Pi-{}^1\Sigma^+$  and not  ${}^1\Sigma-{}^1\Sigma$  as was reported by Sengupta<sup>3</sup>. Recently true potential energy curves and dissociation energies of the ground and excited states of GeO have been calculated by Nair *et al.*<sup>4</sup> using the rotational constants reported by Sengupta. As an exact knowledge is required about the potential energy curves and dissociation energies of the species involved in any phenomena arising from atomic and molecular collisions, an attempt has been made to calculate true potential energy curves and dissociation energies of GeO by using the new data reported by Murthy *et al.* on IBM 1130 computer.

It was shown that the modified Rees Method<sup>5</sup> is as effective as RKR method in giving reliable potential energy curves in many cases. Hence this simple method has been used in evaluating the maximum and minimum turning points in the ground and excited states of GeO molecule. At the same time potential energy curves have also been determined by using Morse<sup>6</sup> analytical potential function to test how far the ( $X^1\Sigma$ ) ground and excited ( $A^1\Pi$ ) states obey Morse potential. It is also known that the difference of the observed rotational constant ' $a_e$ ' from that of the calculated value, according to Pekeris<sup>7</sup> relation, is a measure of deviation from the Morse curve. The calculated and observed values of ' $a_e$ ' and percentage of deviation in the upper and lower states are presented in Table I. As shown in Fig. 1, the true turning

TABLE I

State	$a_e$ observed cm <sup>-1</sup>	$a_e$ calculated cm <sup>-1</sup>	Deviation in the calculated value
$X^1\Sigma^+$	0.0037	0.0020	46%
$A^1\Pi$	0.0034	0.0033	3%

points differ appreciably from those of Morse at higher levels. However, the difference is noticeable at the lower levels also when the deviation in ' $a_e$ ' is more as in the ground state ( $X^1\Sigma^+$ ). For

the excited state ( $A^1\Pi$ ), it can be seen from Fig. 2, that the true curve almost coincides with the Morse curve, since the deviation of ' $a_e$ ' is small. The turning points of fifteen vibrational levels of the lower state and eleven vibrational levels in the upper state are presented in Tables II and III along with their U and U+Te values.

TABLE II

*True potential energy curves of the ground state of GeO*

V	U cm <sup>-1</sup>	$r_{\min}$ (Å)	$r_{\max}$ (Å)
0	489.6	1.572	1.675
1	1466.8	1.541	1.718
2	2436.4	1.520	1.750
3	3395.5	1.504	1.778
4	4348.5	1.491	1.803
5	5289.4	1.480	1.826
6	6223.1	1.470	1.847
7	7148.3	1.462	1.868
8	8061.1	1.454	1.888
9	8969.5	1.447	1.908
10	9869.5	1.440	1.927
11	10758.7	1.434	1.945
12	11641.0	1.428	1.964
13	12513.8	1.423	1.982
14	13377.5	1.418	2.000
15	14231.7	1.414	2.017

Though there are various estimates of dissociation energies proposed by many workers<sup>8-10</sup> there is still considerable divergence between the thermochemical and spectroscopic values. Hence to estimate the dissociation energy, the true potential energy curves of a molecular electronic state have been used, by fitting an empirical potential energy curve to the true potential energy curve. The Hulburt-Hirschfelder and Lippincott three parameter func-

TABLE III

True potential energy curves of the excited state of GeO

$v$	$U \text{ cm}^{-1}$	$U + Te \text{ cm}^{-1}$	$r_{\min} (\text{\AA})$	$r_{\max} (\text{\AA})$
0	324.6	38084.3	1.701	1.827
1	967.6	38727.3	1.662	1.881
2	1600.2	39359.9	1.636	1.921
3	2226.7	39986.4	1.616	1.955
4	2844.4	40604.1	1.600	1.986
5	3455.3	41215.0	1.586	2.014
6	4056.9	41816.6	1.573	2.042
7	4650.4	42410.1	1.562	2.068
8	5238.8	42998.5	1.550	2.095
9	5806.6	43566.3	1.541	2.121
10	6389.1	44148.8	1.534	2.142
11	6955.2	44714.9	1.526	2.165

tions have been shown to fit to a good extent to the true potential energy curves. Recently Szöke and Baitz<sup>12</sup> have proposed a potential energy function which is determined by the electronegativity of the atoms constituting the diatomic molecule.

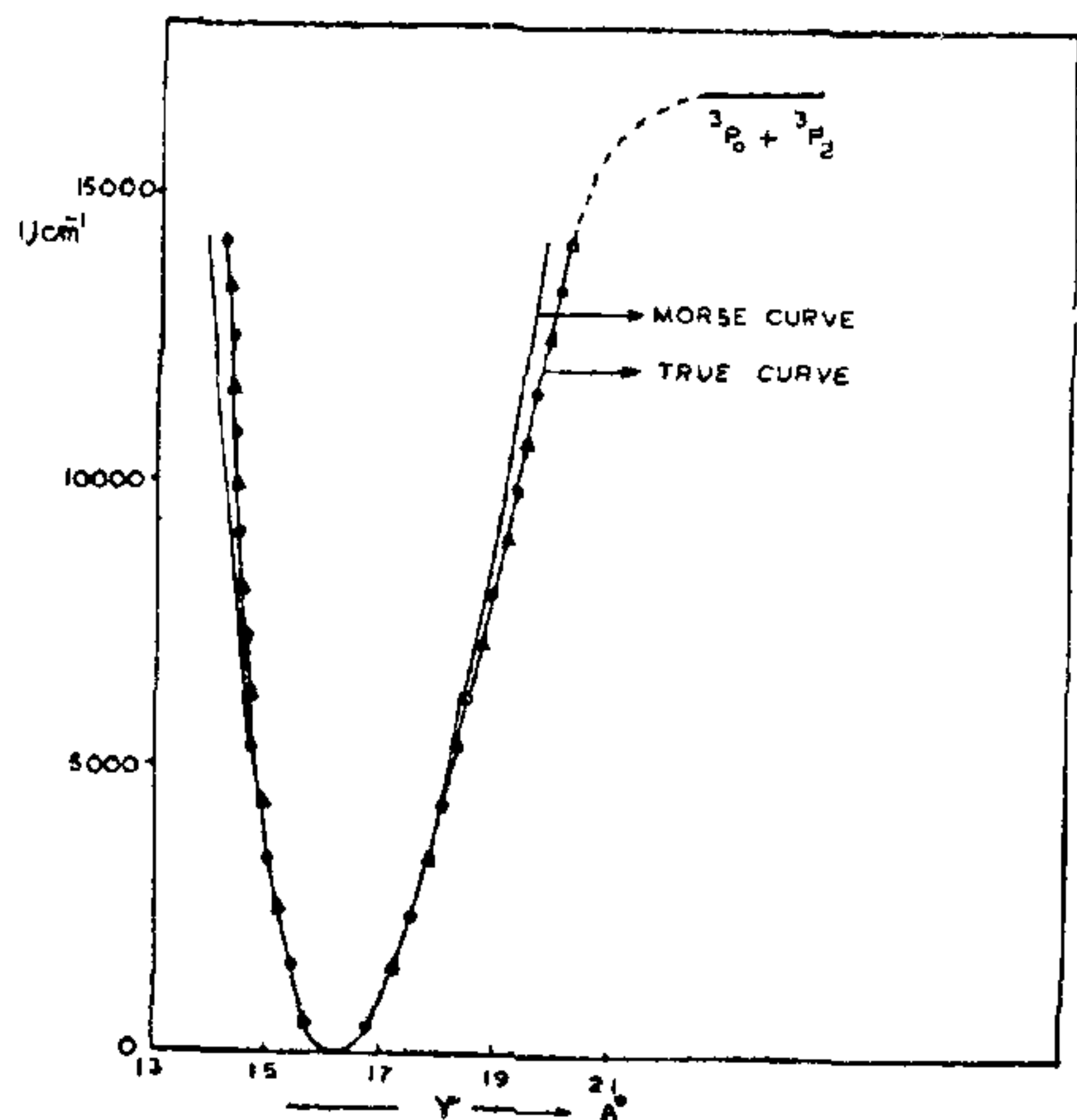


FIG. 1. Potential energy curve of the ground state.  $\Delta$  Electronegativity function.  $\circ$  Lippincott three parameter function.  $\bullet$  Hulbert-Hirschfelder function.

They have shown that this function also gives striking agreement with RKR curves in the case of alkali metal molecules  $\text{Li}_2$  and  $\text{K}_2$ . Hence in the present case the above three functions have been used for the purpose of determining dissociation energy. It is shown in Figs. 1 and 2, that the three functions give reasonable values for the dissociation energies of the ground and excited states of GeO. These dissociation energies calculated in the ground ( $X^1\Sigma$ ) and upper ( $^1\Pi$ ) states are  $33500 \text{ cm}^{-1}$  (4.153 eV) and  $20000 \text{ cm}^{-1}$  (2.479 eV) respectively.

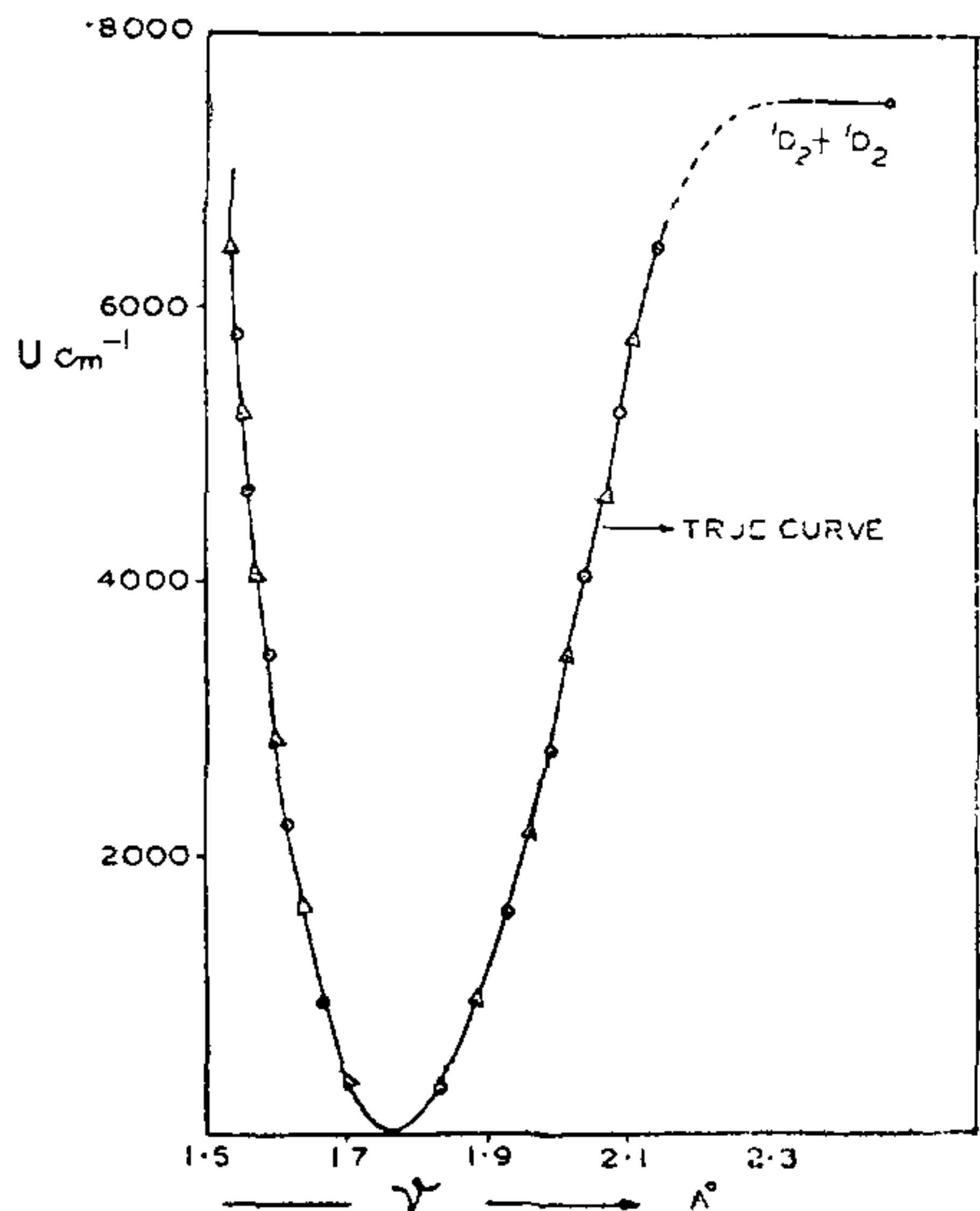


FIG. 2. Potential energy curve of the excited state.  $\Delta$  Electronegativity function.  $\circ$  Lippincott three parameter function.  $\bullet$  Morse curve.

The dissociation products in the upper and lower states are determined as follows. Since

$\text{Te} + \text{De}'(^1\Pi) = \text{De}''(^1\Sigma) + \text{sum of the atomic excitation energies}$ , the sum of the atomic excitation energies is  $24259.7 \text{ cm}^{-1}$  ( $37759.7 + 20,000 - 33,500 = 24259.7 \text{ cm}^{-1}$ ). This is approximately equal to the sum (23,994) of the atomic excitation energies of  $\text{Ge}(^1D_2-7, 126 \text{ cm}^{-1})$  and  $\text{O}(^1D_2-15,868 \text{ cm}^{-1})$ . Thus the GeO molecule gets dissociated in the upper and lower states as

$\text{Ge}(^1D_2) + \text{O}(^1D_2)$  in the upper state and  $\text{Ge}(^3P_0) + \text{O}(^3P_2)$  in the lower state. So it is more probable that the combination of  $\text{Ge}(^1D_2) + \text{O}(^1D_2)$  is responsible for giving an excited ( $^1\Pi$ ) state of GeO molecule. The dissociation energy  $\text{De}''$  in the ground state of GeO estimated to be

TABLE IV  
 r-Centroids of  $A^1\Pi-X^1\Sigma$  system of GeO

$v'/v''$	0	1	2	3	4	5	6		
0 a	1.685	1.712	1.739	1.765	1.793	1.820	1.846		
b	1.684	1.712	1.739	1.766	1.793	1.819	1.845		
c	2659.3	2730.2	2804.2	2882.0	2963.4	3048.4	3137.7		
1 a	1.664	1.694	1.721	1.748	1.775	1.802	1.828		
b	1.665	1.694	1.720	1.748	1.775	1.801	1.827		
c	2614.6	2683.3	2754.8	2829.2	2907.7	2989.7	3075.6		
2 a	1.647	1.675	1.703	1.731	1.757	1.783	1.810		
b	1.647	1.675	1.703	1.730	1.757	1.783	1.809		
c	2575.0	2638.1	2707.6	2779.9	2855.5	2934.3	3017.0		
3 a	1.627	1.657	1.686	1.713	1.739	1.765			
b	1.628	1.657	1.685	1.713	1.739	1.766			
c	2531.2	2595.3	2662.5	2732.2					
4 a	1.608	1.638	1.667	1.696	1.722	1.748			
b	1.609	1.639	1.667	1.695	1.722	1.749			
c	2492.2	2554.5	2619.5	2686.7	2757.5				
5 a	1.589	1.619	1.650	1.678	1.705	1.731			
b	1.589	1.620	1.650	1.678	1.705	1.731			
c	2454.7	2515.0	2578.0	2650.4	2711.8				
6 a	1.568	1.600	1.631	1.660	1.688	1.714			
b	1.569	1.601	1.632	1.660	1.688	1.715			
c	2419.0	2476.7	2538.7	2602.2	2668.3	2737.0			
+5	+4	+3	+2	+1	0	-1	-2	-3	-4
0.011	0.011	0.011	0.010	0.010	0.009	0.009	0.009	0.009	0.009

$\bar{r}_{v',v''}$  values in Å U. (a) graphical method, (b) quadratic equation method, (c) wavelength of the band heads in Å U.

33500  $\text{cm}^{-1}$  (4.153 eV) is considerably lower than the value (6.9 eV) reported by Gaydon.

r-CENTROIDS

The  $\bar{r}$ -centroid ( $\bar{r}_{v',v''}$ ) representing the characteristic internuclear separation of a  $v' \rightarrow v''$  transition in a diatomic molecular band system, has been defined by Nicholls and Jarman<sup>13</sup> as

$$\bar{r}_{v',v''} = \frac{\int \psi_{v'} r \psi_{v''} dr}{\int \psi_{v'} \psi_{v''} dr}$$

where  $\psi_{v'}$  and  $\psi_{v''}$  are the vibrational wave functions and 'r' is the internuclear distance. In the present work, both the graphical and quadratic equation methods (Nicholls and Jarman) have been employed for the evaluation of  $\bar{r}$ -centroids for the bands of  $A^1\Pi-X^1\Sigma$  system of GeO molecule. The results are presented in Table IV. A smooth curve has been obtained when a graph was drawn between  $\bar{r}_{v',v''}$  and  $\lambda_{v',v''}$ . The sequence difference  $\Delta r = \bar{r}_{v'+1,v''+1} - \bar{r}_{v',v''}$  for this system is found to be approximately constant as shown in Table IV.

It is expected that the true potential energy curves presented here will be useful in computing Franck-Condon factors and transition probabilities.

The authors are grateful to Prof. B. R. Rao, Head of the Department of Physics and Director, Computer Centre, Andhra University, Waltair, for granting financial assistance towards computing charges.

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