

THE NEW SYNTHESIS

Nor need biologists 'run scared' of philosophers. Behavioral scientists can no longer escape the involvement of 'purposive action'. The mind should now be accepted as worthy of inquiry by scientific methods (in addition to other methods) and Consciousness has acquired repute and dignity. Perhaps it will do biology a world of good by stepping out a bit to see

what the other non-scientific disciplines are doing to better understand man and the human condition. In this context, eastern philosophies have a great deal to offer. 'The New Synthesis', to be really new and truly a synthesis, should integrate not only biology and sociology; but it should also explore possibilities of identifying areas outside the natural sciences which help in a fuller and more complete understanding of man.

POTENTIAL ENERGY CURVES AND DISSOCIATION ENERGIES OF HYDRIDES, DEUTRIDES, OXIDES AND FLUORIDES OF SOME RARE-EARTH ELEMENTS

B. R. YADAV, S. B. RAI AND D. K. RAI

Spectroscopy Laboratory, Department of Physics, Banaras Hindu University, Varanasi 221 005, India

ABSTRACT

The potential energy curve in different electronic states of LuF, YbF, HoF, TbF, LuH, YbH, LuD, YbD, LuO and PrO have been calculated using RKR method. The dissociation energy of these molecules in their ground state has also been calculated using an empirical electronegativity potential function. The dissociation energy thus obtained has been compared with the other values reported in literature.

1. INTRODUCTION

A KNOWLEDGE of the variation of potential energy of a diatomic molecule with internuclear distance is of fundamental importance in a wide variety of physical problems arising in astrophysics, gas kinetics, chemical reactions, molecular spectra, etc. This widespread applicability has resulted in a very extensive program of obtaining reliable potential energy curves for different electronic states of diatomic molecules. One of the most widely employed and reliable procedures is to make use of the observed energy levels to obtain the classical turning points by a procedure first suggested by Rydberg²³ and by Klein¹⁴. Their graphical procedure was changed into an analytical procedure by Rees²¹ and later by Vanderslice *et al.*²⁴. In the present note we give classical turning points for a number of different electronic states of several diatomic molecules containing rare-earth atoms.

Such studies have been sadly lacking in spite of the importance of rare-earth molecules in a variety of technical applications. Spectroscopic data about the deuterides, hydrides, oxides and fluorides of some of the rare-earth elements have recently become available making such study possible. We have also compared the actual potential energy curve with an empirical function suggested by Szoke and Baitz²⁷ to fix the dissociation energies of the molecules under considerations.

2. METHOD OF CALCULATIONS

The true potential energy curve has been calculated using the RKR method which is in reality a W.K.B.

procedure where one starts with the known energy levels and finds out the classical turning points. The classical turning points r_{min} and r_{max} are given by

$$r_{min} = \left(\frac{f}{g} + f^2 \right)^{1/2} - f$$

$$r_{max} = \left(\frac{f}{g} + f^2 \right)^{1/2} + f \quad (1)$$

where

$$f = \left(\frac{h}{8\pi^2 \mu \omega e x_e} \right)^{1/2} \cdot \ln \left[\frac{(\omega e^2 - 4\omega e x_e U)^{1/2}}{\omega e - (4\omega e x_e U)^{1/2}} \right] \quad (2)$$

$$g = \left(\frac{2\pi^2 \mu c}{h(\omega e x_e)^3} \right)^{1/2} \left[a_0 (4\omega e x_e U)^{1/2} + (2\omega e x_e B_e - a_0 \omega e) \ln \left[\frac{(\omega e^2 - 4\omega e x_e U)^{1/2}}{\omega e - (4\omega e x_e U)^{1/2}} \right] \right] \quad (3)$$

The term U denotes the total energy of vibrational levels and other symbols have their usual spectroscopic meaning. Since in the case of these molecules the rotational vibrational constants of only a few vibrational levels are known, we have used the RKR method where ωe , $\omega e x_e$, B_e and a_0 are taken to be the same for all vibrational levels.

The true potential energy curves for 31 states, viz., $X^1\Sigma$, $A^1\Sigma$, $B^1\Pi$, $E^1\Pi$ and $F^1\Sigma$ states of LuF (Effantin *et al.*⁷; X and A states of HoF (Robbins and Barrow²²; Zmbov and Margrave²⁹); $X^2\Sigma$ and $A^2\Pi_{3/2}$ states

of YbF (Barrow and Chojnicki³; Lee and Zare¹⁸), $X^1\Sigma$, $B^1\Sigma$, $D^1\Pi$ and $G^1\Sigma$ states of LuH (D'Incan *et al.*⁵; Effantin and D'Incan⁶), $X^1\Sigma$, $B^1\Sigma$, $C^1\Pi$ and $H^1\Pi$ states of LuD (Effantin and D'Incan⁷), $X^2\Sigma$, $A^2\Pi_{1/2}$, $E^2\Sigma$ states of YbH and $X^2\Sigma$, $D^2\Pi_{1/2}$, $E^2\Sigma$ and $A^4\Sigma$ of YbD (Kopp *et al.*^{15,16}, Hagland *et al.*¹⁶; Hagland and Kopp¹¹, Hagland¹⁰, Kopp *et al.*¹⁷), X and A states of TbF (Lumbley and Barrow¹⁹), $X^2\Pi$ and $A^2\Lambda$ states of PrO (Shenyavskaya *et al.*²¹; Delaval⁴) and $X^2\Sigma$ and $A^2\Sigma$ states of LuO (Suarez²⁶; Bacis and Bernard²) have been calculated and are given for ground states in Table I*. The molecular constants used in these calculations have been taken from the current references given for the respective molecules.

According to Szoke and Baitz²⁷ a potential function of the form

$$U(r) = D_e \left[1 - \exp\left(-\frac{v \Delta r^2}{2r}\right) \right] \times \left[1 - a \left(\frac{b^2 v}{2r}\right)^{1/2} \Delta r \right] \times \exp\left\{ 1 - \left(\frac{b^2 v}{2r}\right)^{1/2} \Delta r \right\} \quad (4)$$

with

$$d = \frac{U^*(r)}{(e_1 e_2 D_e)^{1/2}}, \quad v = \frac{d \cdot e}{D_e^{1/2}}$$

where $e = (e_1 e_2)^{1/2}$

e_1 and e_2 are electronegativities of the two atoms, a and b are the constants and their values are 0.35 $e^{1/2}$ and 1.065 respectively. This expression is known to represent the potential energy function of a large number of diatomic molecules quite satisfactorily (Singh *et al.*²⁵). Thus if the potential energy term $U(r)$ is known accurately for different r values, the D_e value in the above equation can be adjusted in such a way that the $U(r)$ calculated from this expression fits well with the correct $U(r)$. The dissociation energy thus obtained will be a reasonable estimate of the D_e of the molecule in that particular state. The D_e values obtained in this way for different molecules in their ground state are given in Table II.

3. RESULTS AND DISCUSSION

The diatomic oxides and halides of the rare-earth elements have very deep potential energy minima whereas their hydrides and deuterides show a comparatively shallow minimum. The electronic states of these molecules have high Λ and S values due to the presence of unfilled 4f shells except in case of Lu and Yb where the 4f shell is completely filled.

(i) Hydride, Deutride, Oxide and Fluoride of Lutetium

Lutetium is the last element of the rare-earth series with atomic configuration...4f¹⁴5d¹6s² and the ground state is a regular ²D state. The completed 4f shell takes no part in molecule formation and, therefore, compounds of Lutetium are similar to that of II B group elements (*viz.*, Y, Sc, La) which have... nd¹(n+1)s² configuration.

The ground state of lutetium hydride (deutride) is a ¹ Σ state which arises from the electron configuration (5d⁰6s²) decomposing into...5d¹6s² (Lu: ²D) + 1s (H: ²S) states. The potential energy curves of four states of LuH, *viz.* $X^1\Sigma$, $B^1\Sigma$, $G^1\Sigma$ and $D^1\Pi$ and four states of LuD, *i.e.*, $X^1\Sigma$, $B^1\Sigma$, $C^1\Pi$ and $H^1\Pi$ have been calculated here. The curve fitting method yields the value of D_e , *viz.*, 2.51 eV and 2.55 eV for LuH and LuD respectively. No other estimates are as yet available.

The ground state of LuO is a ² Σ state similar to the ground state of ScO, YO and LaO dissociating into ²D (Lu) + ³P (O). Only one system namely the blue system ($B^2\Sigma - X^2\Sigma$) has been well investigated in this molecule (Suarez²⁶; Bacis and Bernard²) though two more systems lying near 4094 Å and 5170 Å have been predicted by Suarez²⁶. The potential energy curves for these two states B and X have been calculated here. The dissociation energy in the ground state of LuO as estimated by curve fitting comes out to be 5.15 eV. The linear Birge-Sponer extrapolation (from $v = 0$ to $v = 9$) also yields nearly the same value, though Suarez²⁶ using the relation $\omega e^2/4 \omega e x e$ has reported a high value of 6.94 eV. Ackermann *et al.*¹ have given D_e values as 5.34 eV and 6.82 eV for singly ionic and neutral molecule respectively.

Nine electronic states giving rise to eight band systems are known in LuF (Effantin *et al.*⁸). The available data is sufficient for calculation of potential energy curve for $X^1\Sigma$, $A^1\Sigma$, $B^1\Pi$, $E^1\Pi$ and $F^1\Sigma$ states. The rotational analyses have been restricted to bands involving low vibrational quantum numbers and no perturbations have been detected. However the calculated potential energy curves (Fig. 1) indicate that the curve for state A should cross the curve for state B near $v = 5, 6$ of state A and a perturbation is expected in the rotational structure of bands involving these two levels.

LuF is highly ionic molecule and has been estimated to have more than 90% ionic character. The D_e value estimated using electronegativity potential function to represent the potential curve in its ground state is 3.05 eV which is less than the value (4.56 eV) reported by Effantin *et al.*⁸ who used the approximate relation $\omega e^2/4 \omega e x e$. Usually the dissociation energy calculated using this relation in the case of ionic diatomic molecules comes out to be less than the actual value. But it looks surprising that the D_e value

* The data for the other states may be obtained on request from the authors.

TABLE I
Potential energy curves for the hydrides, deuterides oxides and fluorides of some rare-earth elements in their ground states

R (Å)	U (cm ⁻¹)		U (cm ⁻¹)		
	R. K. R.	Elecgy	R. K. R.	Elecgy	
	LuH X ¹ Σ		YbH X ² Σ		
1.4850	10162.5	10167.4	1.6145	7232.4	7192.4
1.5312	7694.5	7678.5	1.6705	5196.5	5160.1
1.5925	5050.5	5037.8	1.7496	2992.2	1978.9
1.6873	2230.5	2228.1	1.9021	619.5	619.9
2.0734	754.5	755.4	2.3888	1826.9	1826.2
2.3194	3662.5	3670.1	2.6206	4115.4	4072.8
2.5043	6394.5	6382.1	2.8249	6235.5	6060.6
2.6751	8950.5	8868.1			
	LuF X ¹ Σ		YbF X ² Σ		
1.6961	6691.3	6623.4	1.7548	6879.1	6672.1
1.7222	5009.5	4947.3	1.7772	5531.7	5394.4
1.7549	3282.6	3250.2	1.8044	4144.7	4065.8
1.8025	1510.8	1504.7	1.8394	2718.2	2685.5
1.8631	304.6	304.0	1.8909	1252.1	1245.9
2.0241	910.3	913.9	2.0818	252.6	252.8
2.1143	2697.0	2704.1	2.2050	1745.1	1739.8
2.1836	4438.8	4442.8	2.2872	3198.1	3167.3
2.2447	6135.6	6115.8	2.3580	4611.5	4527.3
2.3016	7787.4	7726.8	2.4243	5985.3	5815.3
	LuD X ¹ Σ		YbD X ² Σ		
1.5361	7485.7	7311.5	1.6421	6054.9	6078.1
1.5779	5602.8	5500.0	1.6882	4556.5	4560.3
1.6329	3637.5	3597.2	1.7486	2973.6	2971.4
1.7169	1589.8	1581.1	1.8405	1306.12	1304.6
2.0448	535.1	535.0	2.2010	440.6	441.7
2.2418	2624.0	2626.8	2.4224	2150.4	2156.6
2.3844	4630.5	4619.9	2.5851	3775.6	3772.1
2.5114	6554.6	6506.0	2.7321	5316.3	5273.5
2.6314	8396.3	8279.1			
	HoF X (Λ > 2)		TbF X (Ω = 6)		
1.7113	7284.3	7220.3	1.7379	6765.4	6642.7
1.7353	5610.2	5570.0	1.7636	5061.7	4990.6
1.7653	3889.3	3867.4	1.7965	3314.8	3283.6
1.8064	2121.6	2117.0	1.8445	1524.7	1516.9
1.8490	917.0	916.9	2.0190	307.3	307.8
1.9993	306.9	308.0	2.1295	2126.2	2132.2
2.0810	1521.9	1529.1	2.2028	3901.9	3903.6
2.1610	3305.3	3317.3	2.2654	5634.4	5616.5
2.2269	5041.8	5044.0	2.3012	6765.4	6723.9
2.2863	6731.4	6706.10	2.3411	7877.2	7797.0

TABLE I (Contd)

R (Å)	U (cm ⁻¹)		U (cm ⁻¹)	
	R. K. R.	Elecgty	R. K.R.	Elecgty
	LuO X ² Σ		PrO X ² ϕ	
1.5976	7742.9	7773.5	1.5822	9323.1
1.6160	6159.3	6173.6	1.6092	6947.6
1.6378	4550.9	4560.6	1.6430	4532.1
1.6654	2917.7	2922.4	1.6909	2076.7
1.7054	1259.7	1261.0	1.8559	417.5
1.8442	421.4	423.3	1.9001	1249.3
1.9182	2091.8	2098.4	1.9548	2899.6
1.9666	3737.4	3748.8	1.9987	4532.2
2.0104	5358.2	5377.3	2.0545	6947.6
2.0484	6954.2	6974.8	2.0879	8535.7
			2.1193	10106.1
				10121.4

TABLE II

Dissociation energy of some rare-earth molecules

Molecule	Our values (eV)	Value recommen- ded by Gaydon (eV)	Thermochemical value (eV)	Values from other sources (eV)
LuH	2.51
LuD	2.55
LuO	5.15	6.85, 5.34 ^a
LuF	3.05	4.56 ^b
YbH	1.61	1.62 ± .4	..	1.62 ^c
YbD	1.71	1.62 ^c
YbF	2.11	..	4.8	5.00 ^d
HoF	2.98	5.3 ^e
TbF	3.15
PrO	8.55	7.4 ± .3	7.4 ± .3	7.76, 8.23 ^f

^a First value corresponds to neutral molecule and second one to singly ionised as given by Ackermann (1976).

^b Effantin *et al.* (1977) by extrapolation and consideration of dissociation products.

^c Kopp *et al.* (1975) by predissociation in a ⁴Σ state of YbH and YbD.

^d By Lee and Zare (1977) in Chemiluminescence.

^e Zmbov and Margrave (1966).

obtained in present case using this relation is more than our value.

(ii) Hydride, Deutride, Oxide and Fluoride of Ytterbium

The atomic configuration of ytterbium is.... 4f¹⁴ 6s² which resembles the alkaline earth elements. The spectra of YbH and YbD have been studied by Kopp and his co-workers¹⁵⁻¹⁷, and there are six electronic states, *viz*, A ²Π, B ²Σ, C ²Δ, D ²Π, E ²Σ and a ⁴Σ in addition to the ground state X ²Σ which are well characterized.

The ground state of these molecules dissociate into Yb (¹S) + H (²S) while the D ²Π and E ²Σ dissociate into Yb (³P) + H (²S). This is the lowest possible excited dissociation product in YbH or YbD. The combination (³P + ²S) of atomic states gives rise to four molecular states ²Σ, ²Π, ⁴Σ and ⁴Π out of which ²Π and ²Σ can be identified with the D ²Π and E ²Σ states and the ⁴Σ state with the a ⁴Σ state. Kopp *et al.*¹⁷ have surmised that the B and C states in this molecule are not new ²Σ and ²Δ states but are most probably the two components of the ⁴Π state.

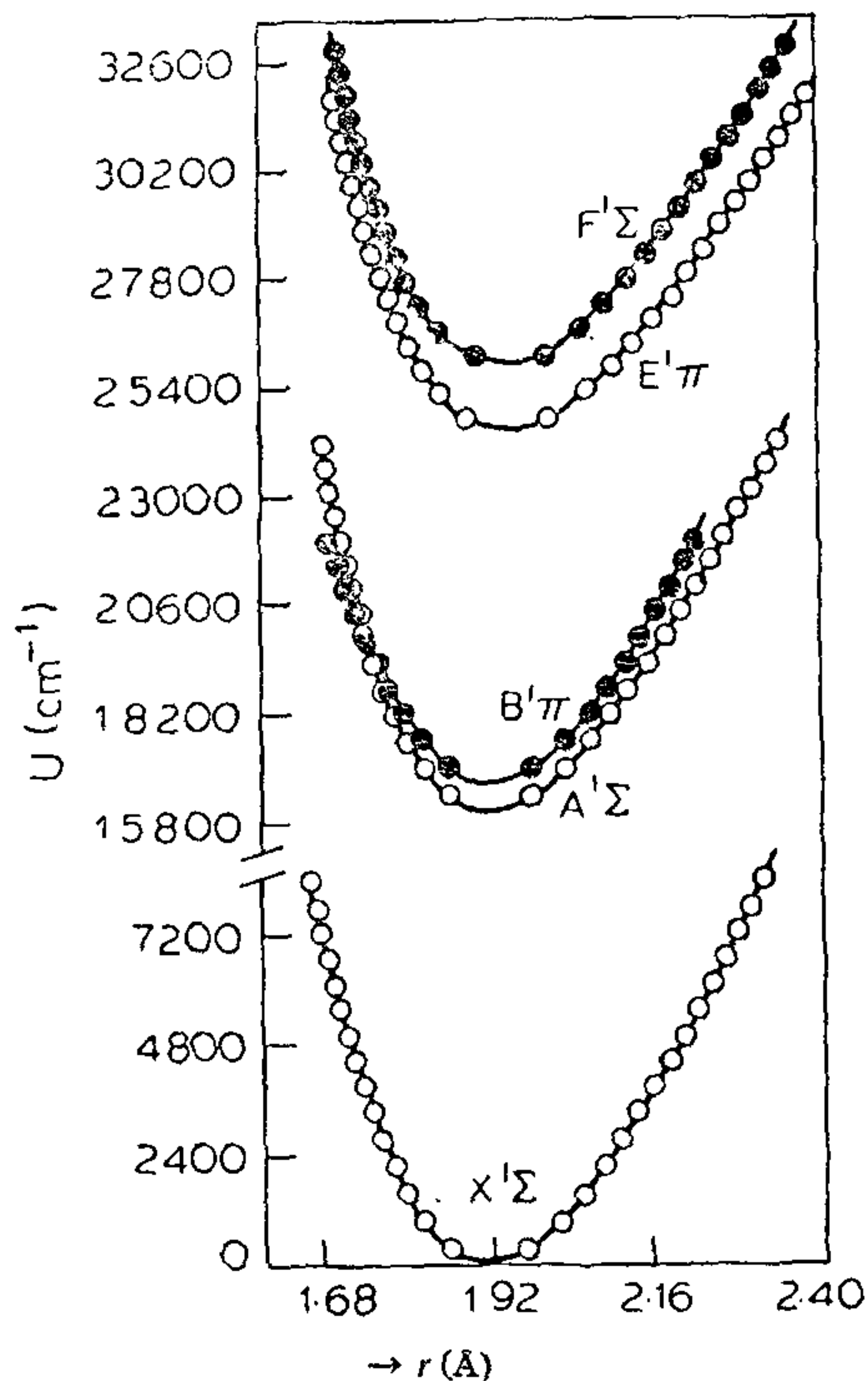


FIG. 1. Potential energy curves for ground and excited states of LuF.

The potential energy curve of three states D, E and X of YbH molecule and four states X, *a*, D and E of YbD has been calculated. It is found that the right limb of the curve for state D of YbH (Fig. 2) crosses the right limb of the curve for the E state near $v = 5, 6$ which is consistent with the perturbations reported in the different vibrational levels of the E state. The rotational structure of the bands involving higher levels of A state has not been studied but it has been reported by Hagland *et al.*¹² that perturbations in E state are due to A state.

The dissociation energy in the ground state of YbH and YbD by curve fitting method is found to be 1.61 eV and 1.71 eV respectively. The linear Birge-Sponer extrapolation in the ground state of ($v = 0-2$) gives a value of 2.2 eV, whereas the value recommended by Gaydon⁹ is 1.61 eV. Kopp *et al.*¹⁷, by a study of predissociation in the $a^4\Sigma$ state of both YbH and YbD, reported a D_e value of 1.62 eV.

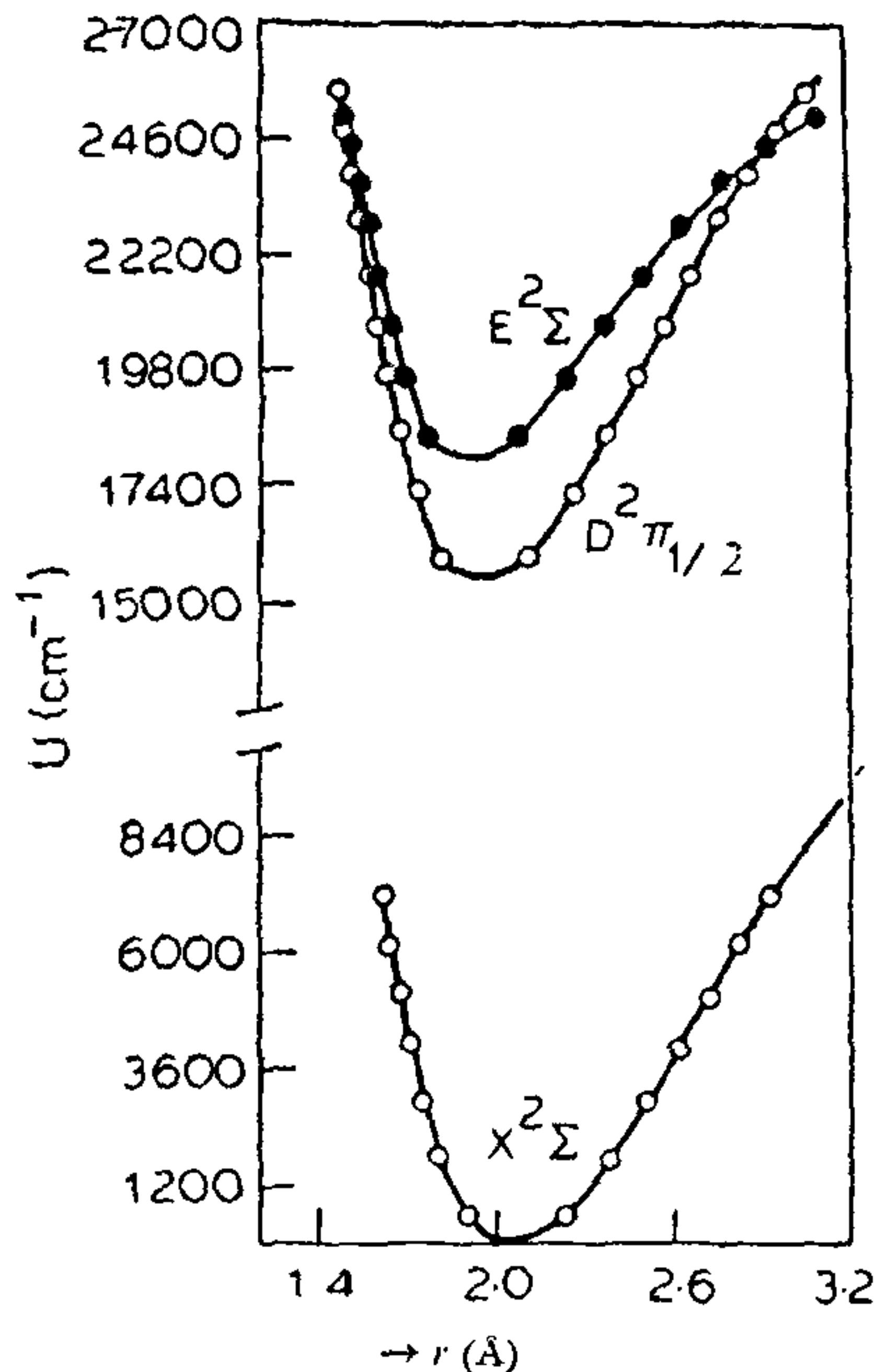


FIG. 2. Potential energy curves for ground and excited states of YbH.

For YbF four electronic states $X^2\Sigma$, $A_1^2\Pi_{1/2}$, $A_2^2\Pi_{3/2}$ and $B(\frac{1}{2})$ are known (Barrow and Chojnicki³; Lee and Zare¹⁸). Since ρ_{exe} is negative in case of $^2\Pi_{1/2}$ and positive for $^2\Pi_{3/2}$ they are referred as A_1 and A_2 states separately. The potential energy curve of only two of these four states namely $A_2^2\Pi_{3/2}$ and $X^2\Sigma$ could be calculated. Due to ionic contribution to the bonding in YbF the ground state can best be represented as $2p \Pi^4 F 6s \sigma_{Yb}$. The curve fitting method estimates the D_0 value in this case as 2.11 eV. A higher value has been reported by Hildenbrand¹⁴ (4.8 eV) and by Lee and Zare¹⁸ (5.0 eV).

(iii) Dissociation Energy of Praseodymium Oxide

A large number of energy states are known in PrO molecule (Shenyavskaya *et al.*²⁰, Delaval⁴). These states lie very close to one another and involve high spin and high Λ values. The ground state of this molecule is a $^2\frac{1}{2}$ state. The potential energy curve of only two states $A^2\Delta$ and $X^2\dot{\sigma}$ could be calculated. The dissociation energy of this molecule by the curve fitting method is found to be 8.5 eV. A comparison of this value with the value obtained by mass-spectrometry (7.4 ± 0.3 eV) (Mavrodineanu and Boiteux²) indicates that

the present value of D_e is high. On the other hand according to Ackermann *et al.*¹, if the molecule formation takes place from ions, the D_e value of this molecule should not be less than 8.23 eV.

(iv) *Dissociation Energy of HoF and TbF Molecules*

Similar to PrO, the energy states in HoF and TbF due to their partially filled 4f shells, are again very complicated. There are two systems A-X and B-X known in holmium fluoride. Robbins and Barrow²² have pointed out that the ground state of this molecule has $\Lambda > 2$ and is most probably an inverted triplet or quintet state. The potential energy curve of the two states X and A have been constructed in the present work. The electronegativity potential energy curve calculation gives D_e value of this molecule as 2.98 eV which is different from the value (5.3 eV) as given by Zmbov and Margrave²⁹.

There are four electronic states and three band systems known in TbF (Lumley and Barrow¹⁹). The lower state of all the three systems is the same and has most probably, $\Omega = 6$. The available data is sufficient only in the case of the X and A states to enable the potential energy curve to be calculated. The dissociation energy in the ground state of this molecule is found to be 3.15 eV. No other estimate is available.

ACKNOWLEDGEMENTS

Authors are grateful to Computer Centre, IIT, Kanpur, for providing computer facility. One of us (B. R. Y.) thanks C.S.I.R., New Delhi, for financial assistance in the form of a S.R.F.

1. Ackermann, R. J., Raug, E. G. and Thorn, R. J., *J. Chem. Phys.*, 1976, **65**, 1027.
2. Bacis, R. and Bernard, A., *Cand. J. Phys.*, 1973, **51**, 648.
3. Barrow, R. F. and Chojnicki, A. H., *J. Chem. Soc. Faraday Trans. II*, 1975, **71**, 728.
4. Delaval, J. M., *Ph.D. Thesis*, L'Universite des Sciences et Technique de Lille, France, 1977.
5. D'Incan, J., Effantin, C. and Bacis, R., *Cand. J. Phys.*, 1972, **50**, 1810.
6. Effantin, C. and D'Incan, J., *Cand. J. Phys.*, 1973, **51**, 1394.
7. — and —, *Ibid.*, 1974, **52**, 523.
8. —, Wannous, G. and D'Incan, J., *Ibid.*, 1977, **55**, 64.
9. Gaydon, A. G., *Dissociation Energies and Spectra of Diatomic Molecules*, Chapman and Hall (London), 1968.
10. Hagland, L., *Ph.D. Thesis*, University of Stockholm, Sweden, 1969.
11. — and Kopp, I., *Ark. Pys.*, 1969, **39** (18), 257.
12. —, — and Aslund, N., *Ibid.*, 1969, **32** (18), 321.
13. Hildenbrand, D. L., *Advances of High Temp. Chemistry*, 1967, **1**, 193.
14. Klein, O., *Z. Phys.*, 1932, **76**, 221.
15. Kopp, I., *Naturwissenschaften*, 1962, **9**, 202.
16. —, *Ph.D. Thesis*, University of Stockholm, Stockholm, Sweden, 1966.
17. —, Hagland, L. and Rydh, B., *Cand. J. Phys.*, 1975, **53**, 2242.
18. Lee, H. U. and Zare, R. N., *J. Mole. Spectry.*, 1977, **64**, 233.
19. Lumley, D. J. W. and Barrow, R. F., *J. Mole. Spectry.* 1978, **69**, 494.
20. Mavrodineanu, R. and Boiteux, H., *Flame Spectroscopy* Wiley, New York, 1965.
21. Rees, A. L. F., *Proc. Phys. Soc. (London)*, 1947, **59**, 998.
22. Robbins, D. J. W. and Barrow, R. F., *J. Phys. B*, 1974, **7**, L234.
23. Rydberg, R., *Z. Phys.*, 1931, **73**, 376; *Ibid.*, 1933, **60**, 514.
24. Shenyavskaya, E. A., Igarova, I. V. and Lupanov, V. N., *J. Mole. Spectry.* 1973, **47**, 355.
25. Singh, J., Nair, K. P. R. and Rai, D. K., *J. Mole. Stru.*, 1970, **5**, 492.
26. Suarez, C. B., *J. Phys. B*, 1970, **3**, 1389.
27. Szoke, S. and Baitz, E., *Cand. J. Phys.*, 1968, **46**, 2563.
28. Vanderslice, J. T., Mason, E. A., Maisch, W. G. and Lippincott, E. R., *J. Mole. Spectry.*, 1959, **3**, 17; *Ibid.* 1960, **5**, 83.
29. Zmbov, K. F. and Margrave, J. L., *J. Phys. Chem.*, 1966, **70**, 3379.

VI INTERNATIONAL CONGRESS OF PROTOZOOLOGY, WARSAW, POLAND

The 6th International Congress of Protozoology will be held in Warsaw, Poland, 5-11 July, 1981. Persons interested may get detailed information at the

following address:

Prof. B. R. Seshachar, Centre for Theoretical Studies, Indian Institute of Science, Bangalore 560 012.