

ON THE DISSOCIATION ENERGY OF GROUP IV-A MONO-SULPHIDES

BY B. P. ASTHANA, ONKAR N. SINGH* AND A. R. SHUKLA

Department of Physics, Banaras Hindu University**

(Received January 29, 1977)

The dissociation energy of diatomic sulphides of group IV-A elements has been computed by fitting the electronegativity potential energy function to the experimental potential energy curves (RKR_V-curves) and the results thus obtained are discussed thoroughly in the light of the ionicity of the bond in question and the limitations of the applicability of different methods to this group of molecules.

1. Introduction

The pressing need to deal with various mysterious molecular processes in space, like aurora glow and aurora borealis etc., has persuaded scientists of diverse fields to probe the quantitative description of these phenomena. However, while attempting to give such a description, it was learnt that, amongst other information, the precise values of the dissociation energy of various diatomic molecules is a must. This has led to various approaches for the precise determination of the dissociation energy of diatomic molecules and a brief account of these approaches showing their relevance to the present study is given in forthcoming sections.

The two general methods which are usually employed to estimate the dissociation energies, make use of the thermochemical and spectroscopic data separately. Of these the spectroscopic data are expected to give rather better results. The thermochemical results are known only for CS [1] and SnS [2] (using $D(S_2) = 4.4$ eV). However, the results using spectroscopic data in various ways (e.g., linear and graphical Birge-Sponer extrapolations, band convergence limit, predissociation, mass-spectroscopic measurements etc.) are available for all the molecules (CS, SiS and PbS; though in each case not by all the methods) chosen for present study. The estimates of the dissociation energies have also

* Present address: U. G. C. (India) Fellow, Section of Physics, Institute of Technology, Banaras Hindu University, Varanasi-221005, India.

** Address: Spectroscopy Laboratory, Department of Physics, Banaras Hindu University, Varanasi-221005, India.

been made by Nair et al. [3] for these molecules using an alternate, rather to say, an indirect spectroscopic method of comparing the experimental potential energy curve with an empirical potential function depending upon the dissociation energy (Lippincott [4] and Hulburt-Hirschfelder [5] function, individually). Recently an empirical potential function has been proposed by Szoke and Baitz [6] which makes use of the electronegativities of the constituent atoms. Calculations using this function were made for CS, SiS and PbS by Singh [7] and for SnS by Ram et al. [8]. But these authors do not appear to have discussed their results in any more detail. For the sake of completeness and to examine the trend all the four sulphides (CS, SiS, SnS and PbS) were taken for the present study and it was thought worthwhile to look rather critically whether or not the ionic consideration plays some important role in the determination of the dissociation energy of these molecules. The present work was, therefore, undertaken this objective as well as with the intention of presenting a comprehensive comparative account of the results obtained by different methods and various approaches.

2. Computational procedure and results

The empirical potential function for diatomic molecules was recently proposed by Szoke and Baitz [6]. Its explicit dependence on the electronegativities of the constituent atoms makes it possible to take due care of the ionicity of the bond formed during molecular formation. The proposed relation is

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

where $v = d_e/D_e^{1/2}$ and a and b are the empirical parameters; a being determined by the relation $a = 0.35 e^{1/2}$ in which $e = (e_1 e_2)^{1/2}$, e_1 and e_2 being the electronegativities of the constituent atoms, b being very nearly the same (~ 1.065) for all diatomic molecules, and d is a constant related to the force-constant (derived from purely spectroscopic data) by the relation

$$k_e = d(e_1 e_2)^{1/2} (D)^{1/2} / r_e.$$

The original procedure of Rydberg [9] which was purely graphical when modified by Klein [10] consisted in evaluating the two integrals $f(u)$, and $g(u)$ in terms of which the classical turning points for any vibration can be given by the relation

$$r_{\min} = (f^2 + f/g)^{1/2} - f, \quad (2)$$

$$r_{\max} = (f^2 + f/g)^{1/2} + f. \quad (3)$$

A modification made by Vanderslice et al. [11], which gives analytical expressions for the evaluation of the $f(u)$ and $g(u)$ integrals, involves essentially a W.K.B. approximation where one starts with the observed vibrational energy levels and from them calculates the two turning points of the corresponding vibration.

TABLE I

Potential energy curves for the ground states of CS, SiS, SnS and PbS molecules

Molecule	RKR				Electronegativity curve	
	v	$U(\text{cm}^{-1})$	$r_{\text{min}}(\text{\AA})$	$r_{\text{max}}(\text{\AA})$	$U_{\text{min}}(\text{cm}^{-1})$	$U_{\text{max}}(\text{cm}^{-1})$
CS ($D_e = 7.25 \text{ eV}$)	0	640.9	1.4827	1.5925	642.9	639.4
	1	1913.7	1.4477	1.6389	1909.6	1928.7
	2	3172.5	1.4251	1.6730	3154.9	3213.6
	3	4418.0	1.4076	1.7021	4379.2	4491.2
	4	5652.5	1.3931	1.7284	5580.7	5764.2
	5	6873.5	1.3805	1.7528	6772.2	7029.0
	6	8084.1	1.3693	1.7759	7953.1	8288.3
	7	9277.7	1.3593	1.7980	9109.3	9539.8
	8	10460.3	1.3501	1.8193	10261.6	10781.3
	9	11628.8	1.3418	1.8399	11376.9	12008.5
	10	12786.1	1.3340	1.8601	12492.7	13231.7
	11	13930.3	1.3267	1.8799	13598.3	14444.8
	12	15063.2	1.3200	1.8993	14666.9	15642.7
	13	16180.0	1.3135	1.9186	15754.0	16839.8
14	17283.6	1.3074	1.9377	16820.6	18026.3	
SiS ($D_e = 6.20 \text{ eV}$)	0	374.1	1.8762	1.9862	373.2	376.6
	1	1118.9	1.8404	2.0315	1104.9	1137.9
	2	1856.6	1.8171	2.0644	1821.0	1900.6
	3	2951.8	1.7989	2.0922	2525.4	2661.9
	4	3323.1	1.7836	2.1172	3223.2	3426.1
	5	4046.4	1.7702	2.1403	3918.0	4191.0
	6	4763.5	1.7584	2.1619	4597.9	4951.4
	7	5478.8	1.7477	2.1825	5271.8	5721.5
	8	6184.4	1.7379	2.2021	5938.7	6465.6
	9	6888.4	1.7289	2.2211	6594.4	7219.2
	10	7590.8	1.7205	2.2396	7244.9	7972.7
	11	8278.1	1.7126	2.2576	7891.7	8722.0
	12	8966.9	1.7051	2.2753	8537.7	9472.4
	13	9649.0	1.6982	2.2924	9160.4	10208.2
	14	10327.4	1.6916	2.3093	9782.0	10944.2
	15	10998.8	1.6850	2.3265	10429.4	11700.6
	16	11666.9	1.6788	2.3433	11061.7	12445.3
	17	12315.4	1.6738	2.3583	11588.9	13113.8
18	12982.5	1.6684	2.3743	12175.9	13829.6	
SnS ($D_e = 4.65 \text{ eV}$)	0	242.6	2.1622	2.2671	205.9	277.3
	1	727.2	2.1276	2.3097	651.5	789.3
	2	1208.8	2.1048	2.3404	1099.9	1293.2
	3	1688.0	2.0869	2.3663	1546.0	1794.3
	4	2164.5	2.0719	2.3894	1987.9	2293.2

TABLE I (cont.)

Molecule	RKR				Electronegativity curve	
	v	U (cm ⁻¹)	r_{\min} (Å)	r_{\max} (Å)	U_{\min} (cm ⁻¹)	U_{\max} (cm ⁻¹)
	5	2638.2	2.0588	2.4106	2427.2	2789.8
	6	3109.1	2.0470	2.4304	2867.5	3283.6
	7	3577.1	2.0364	2.4492	3300.5	3776.7
	8	4043.1	2.0267	2.4672	3729.0	4268.7
	9	4505.8	2.0176	2.4844	4259.8	4755.4
	10	4966.1	2.0092	2.5012	4583.0	5244.7
PbS ($D_e = 3.45$ eV)	0	214.4	2.2352	2.3418	218.2	211.8
	1	641.3	2.2000	2.3851	645.3	641.2
	2	1066.1	2.1769	2.4164	1066.1	1070.9
	3	1487.3	2.1585	2.4430	1488.7	1503.4
	4	1903.9	2.1431	2.4665	1909.1	1930.6
	5	2319.7	2.1300	2.4879	2309.3	2352.3
	6	2735.3	2.1181	2.5081	2715.8	2775.7
	7	3147.1	2.1073	2.5273	3119.2	3198.5
	8	3557.3	2.0973	2.5456	3523.0	3617.9
	9	3963.6	2.0881	2.5632	3921.0	4034.7
	10	4368.9	2.0795	2.5803	4316.8	4450.8
	11	4770.2	2.0714	2.5970	4711.2	4866.4
	12	5168.2	2.0638	2.6132	5100.6	5277.4
	13	5565.7	2.0565	2.6292	5492.8	5689.6
	14	5959.2	2.0496	2.6447	5880.2	6094.1
	15	6348.7	2.0426	2.6607	6290.2	6516.0
	16	6733.7	2.0361	2.6760	6686.4	6923.0

The maximum and minimum points of vibration were calculated for the ground state of CS, SiS, SnS and PbS molecules by Nair et al. [3] using equations (2) and (3) and employing the analytical expressions for $f(u)$ and $g(u)$ integrals as given by Vanderslice et al. [11]. The r_{\min} and r_{\max} thus calculated are fed as such into equation (1) and the best fit of the curve for all the experimentally observed vibrational levels is approached. The best fit has been characterised by near equality of U_{\min} and U_{\max} with U_{RKR} . The value of D_e which gives the best fit with RKR curve is the desired value of dissociation energy for that particular molecule. The agreement between the electronegativity curve and RKR potential energy curve, for the best fit, has been presented in Table I and it has been found that almost all vibrational levels $U(r)$, are reproduced to within an error of 4 to 5%. The results, obtained using the method discussed above, are listed in Table II along with the earlier results, in order to present a comparative account of the various results.

TABLE II

Dissociation energies obtained by different methods for CS, SiS, SnS and PbS molecules in (eV)

Molecule	Herzberg Ref. [24]	Gaydon Ref. [18]	Thermo-Chemical	Mass-spectroscopic	Birge-Sponer Linear Extrapolation for ground state	Empirical potential function* Ref. [3]	Present work	Other methods
CS	7.8	7.6 ± 0.5	7.7 [1]	—	7.8	7.2(L)	7.25	B.S. extrapolation ($v, 0-5$) in the first excited state $A^1\pi$ (perturbed) gives 8.0
SiS	6.6	6.39 ± 0.12	—	—	6.7	5.2(L) 6.6(H)	6.20	G.B.S. extrapolation $D^1\pi (v, 0-10)$ gives 6.4, Convergence limit of state E gives 6.44 ± 0.7 [18]
SnS	3.0	4.8 ± 0.1	4.2 [2]	—	5.2 5.5	4.2(L) 3.0(H)	4.65	L.B.S. extrapolation $B^1\pi (v, 0-7)$ gives 6.1, but the true limit is probably lower; Convergence limit of state E gives 4.8 [18]; continuous absorption of 1770 Å gives 4.7; an onset of predissociation [23] gives 2.97
PbS	4.7	3.5 ± 0.1	—	3.43 [21]	4.3	3.8(L)	3.45	Convergence limit of E system at 2715 Å gives 3.53 [22]

* L and H refer the results obtained using Lippincott [4] and Hulburt-Hirschfelder [5] potential functions respectively.

3. Discussion

3.1. B.S. extrapolation for ground state

The Birge-Sponer extrapolation [12], which is of very general applicability and is most commonly used, is quite easy to perform. However, the method can most suitably be applied for those molecules where the vibrational levels are known right up to the dissociation limit. But there are only a few fortunate cases (like that of the I_2 molecule) where the vibrational levels are observed almost upto the convergence limit. Birge and Sponer [12] have shown that for a large number of molecules it is possible to obtain at least an approximate value for the energy at the limit by extrapolating from the known vibrational levels but the extrapolation values are usually high. There are, however, several

groups of molecules for which this method gives values too low; molecules in which the bonding between two atoms is mainly ionic are typical of this group. If one calculates the percentage ionic characters employing different empirical relations [13–17], for all the four sulphides it comes below 25% in each case. It, therefore, implies that the bonding in these sulphides is primarily covalent in nature. Hence it is evident (from Table II) that a little higher extrapolation value as compared to presently accepted¹ value [18] for these molecules is not beyond expectation. Thus, it appears (from Table II), taking all these into consideration that our values which are a little below the extrapolation value are quite near the true values.

3.2. Thermochemical results

As regards the method of estimating the dissociation energy from thermochemical data, results are available only for CS, and SnS molecules using $D(S_2) = 4.4$ eV. The value as given by Barrow et al. [1] using thermochemical data is 7.7 eV for CS as compared to the presently accepted value of 7.6 eV. Barrow and Rowlinson [2], using corrected higher $D(S_2)$, gives 4.2 eV, for SnS as compared to the presently accepted value of 4.8 eV. Our results for CS and SnS are 7.25 and 4.65 eV, respectively, which are evidently close to the thermochemical results for CS and SnS.

Since the thermochemical results for CS and SnS are based on the value of $D(S_2) = 4.4$ eV, some sort of uncertainty in the value of dissociation energies of CS and SnS might be expected as the value of $D(S_2)$ is also uncertain. However, the value of $D(S_2)$ is rather well established from thermochemical [19] data as well as from an onset of predissociation [20] and is 4.38 eV which is evidently very close to the value used above [$D(S_2) = 4.4$ eV]. Thus it is obvious that no appreciable error is introduced in the thermochemical results due to this very uncertainty. It can, therefore, be emphasized that a considerable amount of reliance can be given to results which are not very far from thermochemical results.

3.3 Other spectroscopic results

Out of the various spectroscopic methods, the mass spectroscopic method is the most reliable one. But unfortunately the mass-spectroscopic [21] result is available only for PbS and is 3.43 eV. The results using the convergence limit of the E state are available for SiS [18], SnS [18] and PbS [22] (please refer Table II) molecules and are 6.44 eV, 4.8 eV and 3.53 eV, respectively. These results are quite close to the experimental results (wherever they are available) as well as the presently accepted values.

The result given by B.S. extrapolation in the A state is 8.0 eV for CS which is higher than the presently accepted value (7.6 eV) as well as the thermochemical value (7.7 eV). This is probably because the A state of CS is perturbed. However, it can readily be seen from Table II that for all the molecules (taken for the present study), our results are in good agreement with the other spectroscopic results. But there is one rather marked discrepancy where Shawhan's [23] prediction of an onset of predissociation in the A state

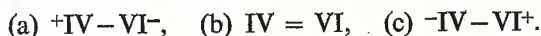
¹ Hereafter the "presently accepted" refers the value recommended by Gaydon in Ref. [18].

gave 2.97 eV for SnS which is too low as compared to our result (4.65 eV). But this discrepancy should now be understood to be resolved as the ($A-X$) system is now known to be badly perturbed. Thus it appears that our values, which are close to the values, obtained from various spectroscopic approaches excepting a few, are fairly reliable for these molecules.

3.4. Results from theoretical considerations

The derivation of dissociation energies from the observations on the lower vibrational and rotational energy levels, is based on a particular potential function model. One of the more interesting potential functions is the Lippincott [4] function which uses the dissociation energy of these molecules as calculated by Nair et al. [3]. Gaydon [18] made a comparison of the results obtained using this method and that by the extrapolation method for the molecules whose dissociation energies are well established and found; while the Birge-Sponer [12] extrapolation is usually too high, the simple Lippincott [4] value is usually too low.

This sort of comparison for group IV- A sulphides, however, reveals that Gaydon's above finding is valid for these molecules. But at the same time it is also evident from Table II that the results obtained by Nair et al. [3] are not too low but they are only a little below the experimental value (wherever it is available). However, it is again evident from Table II that whereas our value for PbS (3.45 eV) is quite close to the mass-spectrometric [21] result (3.43 eV), Nair et al. [3] have reported (3.8 eV) a little higher value as compared to mass-spectrometric result (3.43 eV) for PbS, which therefore seems to be receding farther from Gaydon's above finding. Further, it is to be noted that the difference between presently accepted value and the Lippincott value does not follow any trend. The reason lying behind this irregular feature and also an anomalous result (not in agreement with Gaydon's finding) for PbS using Lippincott function [3] can be sought if one looks for the validity of this function. The Lippincott potential function, since it is based on a δ -function model of binding, is essentially covalent in character. However, the above mentioned irregular feature is not quite unexpected as the Lippincott function [4] being an empirical potential function is not always good representation to the true potential curve (RKR V -curve) and also not very accurate, though the ionic character in going from CS to PbS increases and thereby shows a regular feature. Such an increase in ionic character in going from CS to PbS obvious from the work of Hoeft et al. [25]. Basing on the usual convention of assuming resonance among the three structures (for such molecules)



Hoeft et al. [25], however, argue that in the O, S, Se and Te series, the importance of structure (a) increases in going from C to Pb, which eventually means an increase in ionic character in going from CS to PbS (if we choose "S" from the series). This is also in harmony with the corresponding arguments based on electronegativity by Pauling [26].

The ionic contribution in the case of the PbS molecule, thus becomes rather more appreciable and hence the higher Lippincott value [3] of ~ 3.8 eV as compared to the mass-spectroscopic result [21] (3.43 eV) for PbS might be due to the fact that either Gaydon's

finding is not of general validity or the Lippincott [4] function is no longer a good representation to the true potential energy curve (RKRV-curve) for PbS, whereas it was for lighter molecules.

It is, therefore, quite obvious that our results, which are obtained taking care of the ionicity of the bond and also making use of the spectroscopic data, though not differing by much are more reliable than that given by Nair et al. [3] and are expected to be rather more close to the true value.

The authors are thankful to Dr. C. M. Pathak and Prof. D. K. Rai for their interest in the work. The authors are also thankful to C.S.I.R. and U.G.C., New Delhi (India) for financial assistance during the course of this work.

REFERENCES

- [1] R. F. Barrow, R. N. Dixon, A. Lagerquist, C. V. Wright, *Ark. Fys.* **18**, 543 (1961).
- [2] R. F. Barrow, H. C. Rowlinson, *Proc. R. Soc. A* **224**, 374 (1954).
- [3] K. P. R. Nair, Ran B. Singh, D. K. Rai, *J. Chem. Phys.* **43**, 3570 (1965).
- [4] E. R. Lippincott, R. Schroeder, *J. Chem. Phys.* **23**, 1131 (1955).
- [5] H. M. Hulburt, J. O. Hirschfelder, *J. Chem. Phys.* **9**, 61 (1941).
- [6] S. Szoke, E. Baitz, *Can. J. Phys.* **46**, 2563 (1968).
- [7] J. Singh, Ph. D. Thesis, Banaras Hindu University, 1972.
- [8] R. S. Ram, P. C. Mishra, K. N. Upadhya, *Spectrosc. Lett.* **6**, 544 (1973).
- [9] R. Rydberg, *Z. Phys.* **73**, 376 (1931).
- [10] O. Klein, *Z. Phys.* **76**, 225 (1932).
- [11] J. T. Vanderslice, E. A. Mason, W. G. Maisch, E. R. Lippincott, *J. Mol. Spectrosc.* **3**, 17 (1959); **5**, 83 (1960).
- [12] R. T. Birge, H. Sponer, *Phys. Rev.* **28**, 259 (1926).
- [13] N. B. Hannay, C. P. Smith, *J. Am. Chem. Soc.* **68**, 171 (1946).
- [14] L. Pauling, *J. Phys. Chem.* **56**, 361 (1952).
- [15] J. K. Wilmschurst, *J. Chem. Phys.* **30**, 561 (1959).
- [16] S. S. Batsanov, V. K. Durakov, *J. Struct. Chem.* **2**, 424 (1961).
- [17] W. Gordy, *J. Chem. Phys.* **19**, 792 (1951).
- [18] A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules*, Chapman and Hall Ltd., London 1968.
- [19] J. Drawart, P. Goldfinger, *Quart. Rev. Chem. Soc.* **20**, 545 (1966).
- [20] L. Herman, P. Felenbok, *J. Quant. Spectrosc. Radiat. Transfer* **3**, 247 (1963).
- [21] R. Colin, J. Drowart, *J. Chem. Phys.* **37**, 1120 (1962).
- [22] R. F. Barrow, F. W. Fry, R. C. Le Bargy, *Proc. Phys. Soc.* **81**, 697 (1963).
- [23] E. N. Shawhan, *Phys. Rev.* **48**, 521 (1935).
- [24] G. Herzberg, *Molecular Spectra and Molecular Structure I, Spectra of Diatomic Molecules*, D. Van Nostrand Co., Inc., New York 1950.
- [25] J. Hoefl, F. J. Lovas, E. Tiemann, T. Torring, *J. Chem. Phys.* **53**, 2736 (1970).
- [26] L. Pauling, *The Nature of Chemical Bond*, Oxford and IBH Publishing Co., 1969.