Evaluation of Dissociation Energies of the Diatomic (NdO, FeH and BaF) Molecules

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Abstract
The ground and excited state dissociation energies are determined by curve fitting techniques using the five parameters Hulburt-Hirschfelder (H-H) function. The estimated dissociation energies are 7.33± 0.15eV, 2.90 ± 0.13 eV and 6.04± 0.12eV for NdO, FeH and BaF respectively. The computed values are in good agreement with the literature values. The nature of binding is discussed in the light of the percentage ionic\characters of these molecules.

Keywords: Dissociation energy, Potential energy

Introduction

The Study of Experimental Dissociation energies of diatomic molecules are of great interest in thermochemistry, combustion physics and astrophysics. In quantitative problems of valence, statistical calculations of equilibria at high temperatures, in chemical bonding and in many other problems, the dissociation energy plays a fundamental role. To estimate molecular abundances and interpret dissociation equilibria and ionization process in stellar and in any other astronomical atmospheres, precise dissociation energies and ionization potentials of cemetery molecules are necessary. Spectroscopists and chemists are concerned with determination of reliable values of dissociation energies for the diatomic molecules [1-7]. For a molecular to form and remain stable against dissociation influences in any environment astronomical, chemical etc., the temperature must be sufficiently low and other energetic interactions must be sufficiently mild that the probability of breaking chemical bonds once formed [5,6,8] is low. The formation of a given molecule in the astronomical environment depends mainly on the abundance of the constituent atomic species, the temperature and the physical properties (dissociation energy of the molecule as a fundamental parameter) of the atoms.

Wilkinson [9] has pointed out that knowledge of ionization potentials and dissociation energies is important to astrophysical as

well as many physical and chemical problems. In order to estimate molecular abundances and interpret dissociation equilibria and ionization process in stellar and planetary atmospheres. Precise knowledge of dissociation energies and ionization potentials of astrophysical important molecules are necessary several methods exist in literature to determine bond energies. The procedure to estimate the bond energy is the determination of the energy levels of a molecular species and from these to calculate the energy required to take a single molecule from its lowest possible energy state to the condition in which the constituent atoms can just be removed to an infinite distance apart. The spectroscopic energy of dissociation and the chemical heat of dissociation differ slightly, because the former is calculated at 00C and the latter is calculated at 250C. For measuring large heat of dissociation shockwave method is employed. The method is based on the relationship between the rate of propagation of a shockwave in a gas. i.e., its temperature, pressure and density. Dissociation energies of diatomic molecules are of great interest in thermochemistry, combustion physics and astrophysics. In quantitative problems of valence, statistical calculations of equilibria at high temperatures, in chemical bonding and in many other problems, the dissociation energy plays a fundamental role. To estimate molecular abundances and interpret dissociation equilibria and ionization process in stellar and in any other astronomical atmospheres, precise dissociation energies and ionization potentials of cometary molecules are necessary. Spectroscopists and chemists are concerned with determination of reliable values of dissociation energies for the diatomic molecules [2-7].

Experimental Methods

The experimental knowledge of their molecular parameters and of their electronic structure is of special interest for calculating thermodynamic properties of the corresponding gases. Moreover, rare earth containing diatomic molecules is of astrophysical importance, particularly mono-oxides. The cosmic abundance of Nd is close to that of La and Ce, NdO might be a potential candidate for discovery in cool stellar atmospheres [10]. Precise laboratory data for these molecules should be useful for the interpretation of these complex star spectra. For these reasons many spectral studies of these monoxides have been carried out during the last decade. However, spectroscopic data obtained up to now for NdO are relatively scarce as compared with those for PrO and CeO [11-21].

The most important application of the F $^4\Delta_1$-x $^4\Delta1$ transitions has been found in the spectroscopy of L-type brown dwarfs. Wing and Ford in 1969 [22] have been first to detect a mysterious band near 9910 Å in late M-dwarfs on the basis of low resolution spectra. The Wing Ford bond was later found in S-stars [23] and in sunspots at higher spectral resolution. Wing and Brault [24] identified the 0-0 band of a FeH electronic transition by comparison with an unassigned laboratory spectrum of FeH that showed a head at 9896 Å [25] and this band is also seen in sunspots [24] and identified as 2-0 and 2-1 bands. FeH band can be observed well past 1μm with the 0-1 band of the F $^4\Delta_1$–X $^4\Delta_1$transition easily visible near 1.19 μm in sunspots. A new electronic transition of FeH has been identified near 1.583 μm in late M-dwarfs and sunspots. Laboratory spectra of the 1-0 band of this FeH transition show a head at 8691Å and this band is also seen in sunspots Wing and brault [24]. Dulick et al [26] calculated the new spectrometer line lists and opacities for the F$^4\Delta_1$-x$^4\Delta_1$ transition of FeH and emphasized that 0-0 band of this transition is responsible for the Wing-Ford band observed in M-type stars, sunspots and brown dwarfs.

Molecular beam optical Stark and Zeeman study of the A $^2\prod_r$ -X $^2\Sigma+$ (0,0) band system of BaF has been recorded using high resolution laser induced florescence spectroscopy by Steimle et al [27]. Laser excited florescence and thermal emission spectra of BaF molecule have been analyzed by Effantin et al [28]. Thermally excited emission spectra of barium mono fluoride have been identified and respective vibrational analysis carried out [29]. Kenan [30] has been found four

strong bands in the wavelength region 800-900Å appearing in S stars. Lindgreen and Glofsson [31] discussed the identification problem of the IR "Keenan bands" in S stars. Wyckoff and Clegg [32] have been found medium-resolution spectrogram of the S stars.

The molecular constants required for the present study have been taken from literature [33–39] and are listed in Table 1.

Table 1 Spectroscopic Molecular Constants for Different Electronic States of the Diatomic Molecules

Molecule	μ	State	T_e (cm^{-1})	ω_e (cm^{-1})	$\omega_e X_e$ (cm^{-1})	B_e (cm^{-1})	α_e (cm^{-1})	r_e (Å)
NdO	14.3746	X (1)4	0(1654)	834.083	2.2855	0.362	0.0014	1.7991
		(1)3	1980.29	824.243	2.07c	0.352	0.0012	1.8236
		[10.935]4	10935.33	808.925[b]	1.91[c]	0.344	0.0011	1.8460
FeH	0.9899	X$^4\Delta$	315.879	1833.36	35.53	6.566	0.1639	1.6105
		F$^4\Delta$	10313.11	1498.84	37.47	5.988	0.2082	1.6861
BaF	16.698	X$^2\Sigma+$	0	468.9	1.79	0.215	0.0012	2.126
		A $^2\prod_r$	11646.9	436.7	1.82	0.211	0.0012	2.183

μ = Reduced mass, T_e= Electronic energy above ground state (cm^{-1}), ω_e = Vibrational spacing (cm^{-1}), $\omega_e x_e$ = Anharmonic correction to vibrational spacing (cm^{-1}), B_e = Rigid rotator rotational spacing (cm^{-1}), α_e = Non rigid rotator correction to B_e(cm^{-1}), r^e= Equilibrium inter nuclear distance (A^o).

Potential Energy Curves

Experimentally observed vibrational levels are used to construct the potential energy curve. Many authors employed this method and constructed the potential energy curves [40–43]. The RKRV [44-48] method is an improved form of RKR method, which makes use of Wentzel–Kramers–Brillouin (WKB) approximation from which we obtain reliable potential energy curves with the observed vibrational and rotational constants. The potential energy curves are constructed using the method of RKRV [44-48] utilizing the above molecular constants.

Dissociation Energy

The RKRV turning points are inserted into the five parameter Hulburt–Hirschfelder [49,50] function and the energies U(r) are calculated by varying the D_e values. An average percentage deviation is determined between the calculated U(r) and the experimental G(υ) values. An accurate estimation of the dissociation energy (D_o) requires an empirical potential function, which provides the best reproduction of the experimental energy values. A critical evaluation of the importance of these functions was given by Steele et al. [51] and they have shown that the potential function of Hulburt–Hirschfelder (H–H) [49,50] fits well with the RKRV curves of a large number of diatomic molecules. In the present investigation, it is observed that the H–H [49,50] function fits best and reproduces the experimental energy values. Different De values are used in the H–H function and the De value, for which the best fit of the energy values U(r) is observed, which is taken as the dissociation energy (D_e) of the molecule.

Table 2 Energy values obtained from Hulburt–Hirschfelder (H-H) function for the X (1)electronic state of NdO molecule

r (A°)	U (cm⁻¹)	U(r)cm⁻¹		
		D_e =7.30eV	D_e =7.33eV	D_e =7.35eV
1.854	416.47	415.11	416.52	417.93
1.897	1245.98	1242.14	1246.36	1250.58
1.928	2070.92	2065.05	2072.06	2079.07
1.954	2891.29	2884.09	2893.87	2903.66
1.977	3707.09	3699.16	3711.72	3724.28
1.999	4518.32	4510.57	4525.88	4541.19
2.019	5324.97	5318.05	5336.10	5354.15
2.038	6127.06	6121.99	6142.77	6163.55
2.056	6924.57	6922.36	6945.85	6969.35
1.747	416.47	415.07	416.48	417.88
1.712	1245.98	1241.55	1245.77	1249.98
1.689	2070.92	2063.02	2070.02	2077.02
1.671	2891.29	2879.18	2888.95	2898.72
1.656	3707.09	3690.08	3702.60	3715.13
1.642	4518.32	4495.42	4510.68	4525.94
1.630	5324.97	5295.46	5313.43	5331.41
1.620	6127.06	6089.75	6110.42	6131.09
1.610	6924.57	6878.30	6901.65	6925.00
Average percentage deviation		0.34	0.14	0.33

Table 3 Energy Values Obtained from Hulburt–Hirschfelder (H-H) Function for the X⁴Δ Electronic State of FeH Molecule

r (A°)	U (cm⁻¹)	U(r)cm⁻¹		
		D_e =2.87eV	D_e =2.90eV	D_e =2.92eV
1.759	907.79	891.77	899.45	907.13
1.992	4361.33	4317.71	4354.90	4392.10
2.085	5981.51	5960.18	6044.52	6062.86
2.174	7530.63	7565.21	7630.38	7695.54
0.022	9008.69	9140.18	9318.91	9297.65
2.346	10415.70	10692.61	10784.71	10876.82
2.433	11751.64	12230.53	12335.88	12441.23
2.521	13016.52	13763.15	13881.70	14000.26
1.485	907.79	890.77	898.45	906.12
1.406	2670.09	2615.72	2638.25	2660.78
1.357	4361.33	4263.72	4300.45	4337.18

1.320	5981.51	5834.67	5884.93	5935.19
1.289	7530.63	7329.26	7392.39	7455.52
1.263	9008.69	8748.42	8823.78	8899.14
1.240	10415.7	10093.56	10180.50	10267.45
1.219	11751.64	11366.21	11464.12	11562.03
1.200	13016.52	12567.86	12676.11	12784.37
Average percentage deviation		2.38	0.13	1.91

Table 4 Energy Values Obtained from Hulburt–Hirschfelder (H-H) Function for the $X^{2\Sigma+}$ electronic state of BaF molecule.

r (A°)	U (cm⁻¹)	U(r)cm⁻¹		
		D_e =6.02eV	D_e =6.04eV	D_e =6.07eV
2.193	234.00	232.91	233.87	234.83
2.247	699.32	695.97	698.84	701.71
2.286	1161.06	115.30	1160.06	1164.81
2.319	1619.22	1610.86	1617.49	1624.13
2.349	2073.80	2062.51	2071.00	2079.49
2.376	2524.80	2510.48	2520.81	2531.15
2.402	2972.22	2954.53	2966.69	2978.86
2.427	3416.06	3394.83	3408.81	3422.79
2.451	3856.32	3831.34	3847.11	3862.89
2.064	234.00	232.94	233.90	234.86
2.022	699.32	696.31	699.17	702.04
1.995	1161.06	1156.43	1161.19	1165.95
1.974	1612.22	1613.44	1620.08	1626.73
1.956	2078.80	2067.58	2076.09	2084.61
1.941	2524.80	2518.72	2529.09	2539.46
1.927	2972.22	2967.19	2979.40	2991.62
1.915	3416.06	3412.92	3426.97	3441.02
1.904	3856.32	3856.07	3871.95	3887.83
Average deviation percentage		0.40	0.12	0.41

Results and Discussion

The inherent error in the H–H function given by Steele et al. [51] is 2%. The error involved in the evaluation of D_e is the average percentage deviation plus the inherent error in the potential function. Employing the Hulburt-Hirschfelder's [49] potential function, the D_e value for the ground state of NdO molecule has been evaluated. The relevant U(r) values for the selected De values are given in the Table 2. For the molecule NdO it is obvious from Table 2 that the best fitting of the energy value is achieved for D_e = 7.33 eV. Since the average percentage deviation in this case is minimum 0.14. Hence, the dissociation energy for the ground state of NdOis 7.33 eV and the value as measured from the lowest vibrational levels is D_0 = 7.33±0.15 eV. The estimated D_0 value

for NdO (7.33±0.15 eV) is in close agreement with the value7.33eV recommended by Huber and Herzberg [52].

The obtained Do value is 2.90 eV for FeH. The Do for which the best fit obtains is taken to be the dissociation energy of the molecule. This value is in good agreement with the value 2.93eV [52] quoted by Huber and Herzberg. The observed energy values have been compared with the calculated energy values are presented in Table 3.

For the molecule BaF, it is obvious from Table 4 that the best fitting of the energy value is achieved for D_e=6.047 eV. Since the average percentage deviation in this case is minimum (0.12). The dissociation energy for the ground state of BaF is 6.047 eV and the value as measured from the lowest vibrational level is D_0 = 6.04 ± 0.12 eV. i.e. D_0=De- G (0). The estimated D_0 value 6.04 ± 0.12 eV for BaF is in good agreement with the value 5.98 eV listed by Zygmunt et al [53] and fair in agreement with the Huber and Herzberg [52] quoted value 6.05 eV.

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