

On the dissociation energy of MgH^+ molecule

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Abstract. The true potential energy curve for the electronic ground state, $X^1\Sigma^+$, of MgH^+ molecule has been constructed by the Rydberg-Klein-Rees method as modified by the method of Vanderslice *et al.* Empirical potential functions, of five-parameters by Hulburt and Hirschfelder, of three-parameters by Lippincott and others, and, of electronegativity by Szöke and Baitz, are examined for the adequacy to represent the true curve. The electronegativity function is found to be the best fitting function and the dissociation energy is estimated whose order is verified by the force constant.

Keywords. MgH^+ molecule; true potential energy curve, dissociation energy; electronegativity function; curve fitting method.

1. Introduction

The bond dissociation energy of a diatomic molecule is the most direct measure of the strength of the bond, and therefore of the stability of the chemical combination between the constituent atoms, that is, the very existence of the molecule. Astrophysicists, chemists and spectroscopists are therefore concerned with the determination of reliable values of dissociation energies for diatomic molecules.

Balfour (1972) reports that the $A^1\Sigma^+ - X^1\Sigma^+$ transition of MgH^+ is reasonably strong and it therefore seems possible that MgH^+ is present in a detectable amount in the solar spectrum.

The graphical Birge-Sponer extrapolation of vibrational levels in $X^1\Sigma^+$ and $A^1\Sigma^+$ states gives the dissociation energy D_0^0 value of MgH^+ as 2.08 eV (Huber and Herzberg 1979). Balfour (1972) has arrived at the D_0^0 value of MgH^+ as 2.23 eV from the ionization potential.

The curve fitting method is found to yield reliable values for the dissociation energies of a large number of diatomic molecules (Rajamanickam *et al.* 1982a, b; Narasimhamurthy and Rajamanickam 1983; Rajamanickam and Narasimhamurthy 1983; Rajamanickam 1985). The procedure consists of determining the D_e parameterised empirical potential function which best fits the true potential energy curve for the electronic ground state of the molecule. Many empirical potential functions are known for diatomic molecules. Of those, functions given by Lippincott *et al.* (1961) in the modified form, by Hulburt and Hirschfelder (1941) and, by Szöke and Baitz (1968) describe adequately the potential energies of many molecules. These functions are therefore examined in the present study to estimate the dissociation energy for the electronic ground state, $X^1\Sigma^+$, of MgH^+ from the constructed true potential energy curve.

2. True potential energy curve

Experimentally observed vibrational levels are used to construct the true potential energy curve. For the known vibrational levels, the Rydberg-Klein-Rees (RKR) method gives the turning points by

$$r_{\pm} = [(f_v/g_v) + f_v^2]^{1/2} \pm f_v, \quad (1)$$

where f_v and g_v are calculated by the procedure of Vanderslice *et al* (1960). The molecular constants (Huber and Herzberg 1979) used in the present study are listed in table 1. In table 2, the computed values of the turning points are given for the molecular vibration in the electronic ground state of MgH^+ .

Table 1. Molecular constants for the electronic ground state, $X^1\Sigma^+$ of MgH^+ molecule.

ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	$\omega_e y_e$ (cm^{-1})	B_e (cm^{-1})	α_e (cm^{-1})	r_e (Å)	Electronegativities*	
						e_1	e_2
1699.1	31.935	-0.1882	6.387	0.18194	1.6519	1.2	2.1

Huber and Herzberg 1979; *Pauling (1960).

Table 2. Energy values from the EN function for MgH^+ molecule.

v	r_{\pm} (Å)	$G(v)$ (cm^{-1})	$U(r)$ cm^{-1}		
			$D_e = 2.1$ eV	$D_e = 2.15$ eV	$D_e = 2.2$ eV
0	1.8107	841.54	847.20	848.57	849.63
1	1.9498	2476.16	2494.52	2502.04	2508.77
2	2.0597	4045.20	4078.78	4088.20	4104.34
3	2.1597	5547.56	5571.89	5602.83	5631.93
4	2.2551	6982.12	6982.56	7030.40	7075.83
5	2.3494	8347.71	8307.42	8375.52	8440.57
6	2.4432	9643.24	9524.21	9615.22	9702.82
7	2.5397	10867.56	10650.91	10767.71	10880.55
8	2.6376	12019.55	11657.10	11801.28	11940.98
0	1.5220	841.54	833.74	832.69	832.02
1	1.4412	2476.16	2448.15	2443.90	2440.53
2	1.3917	4045.20	3992.58	3984.88	3978.04
3	1.3545	5547.56	5480.46	5468.79	5458.76
4	1.3245	6982.12	6908.03	6892.78	6879.37
5	1.2988	8347.71	8307.19	8288.23	8271.74
6	1.2766	9643.24	9652.93	9630.87	9611.13
7	1.2562	10867.56	11009.51	10984.12	10961.56
8	1.2381	12019.55	12317.75	12289.50	12264.16
Average percentage deviation			1.07	1.04	1.14

3. Electronegativity function

Szöke and Baitz (1968) have constructed the electronegativity (EN) potential energy function, with the aid of parameters other than spectroscopic constants, to link different areas in chemical physics and they have replaced the force constant k_e of a diatomic molecule by an expression connected with the Pauling (1960) electronegativities e_1, e_2 as

$$k_e = d(e_1 e_2 D_e \times 1.60199 \times 10^{-12})^{1/2} r_e^{-1}, \quad (2)$$

And the EN function is in the form

$$U(r) = 8068.3 D_e [1 - \exp\{-v(r - r_e)^2/2r\}] \\ \times [1 - a(b^2 v/2r)^{1/2}(r - r_e) \exp\{-(b^2 v/2r_e)^{1/2}(r - r_e)\}], \quad (3)$$

where

$$v = de/(D_e \times 1.60199 \times 10^{-12})^{1/2},$$

$$d = 5.8883 \times 10^{-2} \mu_A \omega_e^2 r_e / (e_1 e_2 D_e \times 1.60199 \times 10^{-12})^{1/2},$$

$$a = 0.35 e^{1/2}, e = (e_1 e_2)^{1/2} \text{ and } b = 1.065.$$

4. Dissociation energy

For the constructed true potential energy curve, the energies $U(r)$ are calculated with the empirical potential functions by varying the D_e value. An average percentage deviation is determined between the calculated $U(r)$ and the experimental $G(v)$ values. The dissociation energy from any function is that value of D_e which gives the least deviation. The function leading to smallest deviation determines the dissociation energy of the molecule. The dissociation energy referred to $v = 0$ level is given by $D_0^0 = D_e - G(0)$.

This procedure is applied to determine the adequacy of the empirical potential functions (Lippincott *et al* 1961; Hulburt and Hirschfelder 1941; Szöke and Baitz 1968) to represent the electronic ground state of MgH^+ . D_e is varied over a range of 1.5 to 3.0 eV in steps of 0.05 eV. The EN function leads to the dissociation energy of MgH^+ , as the deviation is the least. Only relevant results of $U(r)$ are given in table 2. The estimated dissociation energy for the electronic ground state of MgH^+ is 2.05 ± 0.02 eV. The error indicated in the result takes into account the error of 1.04% involved in the curve fitting.

5. Conclusions

The results of the present study are significant since the EN function is suited for the MgH^+ molecule. The estimated dissociation energy $D_0^0 = 2.05 \pm 0.02$ agrees to within 2% of the value $D_0^0 = 2.08$ eV of Huber and Herzberg (1979). The force constant for the ground state of MgH^+ also indicates that the dissociation energy obtained in the present study is of the correct magnitude.

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