POTENTIAL ENERGY CURVE AND DISSOCIATION ENERGY FOR THE SnCl MOLECULE

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The potential energy curve for the electronic ground state of the SnCl molecule has been constructed by the Rydberg–Klein–Rees method in the modification by Vanderslice and collaborators. Empirical potential functions, of five parameters by Hulburt and Hirschfelder, of three parameters by Lippincott and collaborators, and that by Szöke and Baitz using the electronegativity are examined for their adequacy to represent the true curve. The five parameter Hulburt–Hirschfelder function, $U(r) = D_e\,[(1 - e^{-x})^2 + c\,x^3 e^{-2x}(1 + b\,x)]$, was found to be the best fitting function and it was used for the determination of the dissociation energy. The estimated value attained for dissociation energy is 346 ± 8 kJ mol^{-1}. For this value of dissociation energy, the estimated values for the parameters and expansion coefficients are $c = 0.06864$, $b = -0.363738$, $a_0 = 2.759 \,.\, 10^3$ m^{-1}, $a_1 = 2.876$ and $a_2 = 4.013$, a_0, a_1 and a_2 being the Dunham's coefficients.

In recent years experimental potential energy curves have been constructed for many diatomic species which are of interest in various fields such as astrophysics, gas kinetics and aerodynamics. A detailed knowledge of potential energy curves helps in the determination of Franck–Condon factors and r-centroids which are needed for testing intensity theories, such as the variation of electronic transition moment with the internuclear separation, a knowledge of which is lacking for many diatomic molecules of astrophysical and general interest. The experimental curve may be used as a standard for selecting such an empirical potential function which best fits the molecular electronic state. In particular, the dissociation energy may be estimated reliably from the empirical function describing adequately the electronic ground state. Many methods are available to construct the true potential energy curve using experimental data. The

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approach of Rydberg–Klein–Rees (RKR) as modified by Vanderslice et al.[1] is the one largely employed.

For a molecular species to be formed and remain stable against dissociating influences in any environment, astronomical or chemical, the temperature must be sufficiently low and other energetic interactions must be sufficiently mild so that the probability of breaking chemical bond once formed is low. The dissociation energy of diatomic molecules is of primary importance in such phenomena and astrophysicists, chemists and spectroscopists are concerned about its reliable determination. The curve fitting method has been found to yield reliable values for the dissociation energies of a large number of diatomic molecules[2 – 15]. The procedure consists in determining the D_e-parameterised empirical potential function which best fits the true potential energy curve for the electronic ground state of the molecule.

To our best knowledge, there has been no report on the true potential energy curve and the experimental dissociation energy for the electronic ground state of the SnCl molecule[16]. As far as theoretical calculations are concerned, Balasubramanian[17] has carried out an self-consistent field with relativistic configuration interaction calculation on SnCl and obtained theoretical values for the equilibrium bond length and dissociation energy for some molecular electronic states. Experimental energy levels are known[18] up to the vibrational quantum number $v = 11$. A reliable true potential energy curve can therefore be constructed. In the present work we adopt the RKR method.

Many empirical potential functions are known for diatomic molecules. Of these, the three parameters modified Lippincott function[19], the five parameter Hulburt–Hirschfelder function[20], and that using the electronegativity according to Szöke and Baitz[21] describe the potential energies of many molecules adequately. These functions are therefore examined in the present study to estimate the dissociation energy of the electronic ground state of SnCl from the constructed true potential energy curve.

RESULTS

True Potential Energy Curve

Experimentally observed vibrational levels are used to construct the true potential energy curve. For the known vibrational levels, the RKR method gives the turning points by

$$r_{\max} = [(f_v/g_v) + f_v^2]^{1/2} + f_v \qquad (1)$$

$$r_{\min} = [(f_v/g_v) + f_v^2]^{1/2} - f_v , \qquad (2)$$

where f and g are calculated by Vanderslice's procedure[1]. The molecular constants[16] used in the present study are listed in Table I. The computed values of the turning points are given in Table II for the molecular vibrations in the electronic ground state of SnCl.

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 the smallest deviation determines the dissociation energy of the molecule. The dissociation energy referred to $v = 0$ level is given by $D_0^o = D_e - G(0)$.

This procedure is applied to determine the adequacy of the empirical potential functions[19 - 21] to represent the electronic ground state of SnCl. D_e is varied over a range from 320 kJ mol^{-1} to 364 kJ mol^{-1} in steps of 1 kJ mol^{-1}. In this range, the results attained from Lippincott function along with Szöke and Baitz function show a larger deviation from the $G(v)$ values than those obtained from Hulburt–Hirschfelder function. Likewise, when going to higher v, they show an increasing monotonic trend without any inflection point in the percentage deviation with respect to $G(v)$. Therefore, only the Hulburt–Hirschfelder function leads clearly to the dissociation energy of SnCl. For this reason, only the results of $U(r)$ from the Hulburt–Hirschfelder potential function are given in Table II. The estimated dissociation energy, D_e, for the electronic ground state of SnCl turns out to be 346 ± 8 kJ mol^{-1}. The error indicated in the result takes into account the error of 2% inherent in Hulburt–Hirschfelder function[22] and the error

TABLE I
Molecular constants[16] for the ground state of SnCl

Constant[a]	Value[b]
ω_e	351.1
$\omega_e x_e$	1.06
B_e	0.117
α_e	0.0004
r_e	2.361
e_1	1.8
e_2	3.0

[a] e_1 and e_2 are Pauling's electronegativities. [b] ω_e, $\omega_e x_e$, B_e and α_e are in cm^{-1}, r_e is in 10^{-10} m.

involved in the curve fitting. For this value of dissociation energy, the estimated values for the parameters and expansion coefficients (depending on D_e) are $c = 0.06864$, $b = -0.363738$, $a_0 = 2.759 \cdot 10^3$ m^{-1}, $a_1 = 2.876$ and $a_2 = 4.013$, a_0, a_1 and a_2 being the Dunham's coefficients.

TABLE II
Energies given by the Hulburt–Hirschfelder function for the electronic ground state for SnCl molecule for three assumed values of D_e[a]

v	r, 10^{-10}m	$G(v)$, kJ mol^{-1}	$\lvert G(v) - U(r)\rvert$, kJ mol^{-1}		
			A	B	C
0	2.4232	2.0969	0.0255	0.0255	0.0255
1	2.4715	6.2716	0.0413	0.0414	0.0414
2	2.5063	10.4210	0.0489	0.0493	0.0495
3	2.5356	14.5450	0.0519	0.0527	0.0532
4	2.5618	18.6436	0.0507	0.0523	0.0533
5	2.5858	22.7169	0.0455	0.0481	0.0499
6	2.6083	26.7648	0.0368	0.0408	0.0437
7	2.6296	30.7873	0.0246	0.0304	0.0346
8	2.6500	34.7845	0.0084	0.0164	0.0221
9	2.6695	38.7563	0.0106	0.0005	0.0072
10	2.6885	42.7028	0.0350	0.0212	0.0112
11	2.7069	46.6239	0.0627	0.0451	0.0325
0	2.3039	2.0969	0.0279	0.0279	0.0279
1	2.2643	6.2716	0.0484	0.0486	0.0486
2	2.2382	10.4210	0.0604	0.0606	0.0609
3	2.2176	14.5450	0.0665	0.0671	0.0676
4	2.2003	18.6436	0.0671	0.0682	0.0689
5	2.1851	22.7169	0.0616	0.0634	0.0646
6	2.1716	26.7648	0.0505	0.0532	0.0550
7	2.1592	30.7873	0.0336	0.0373	0.0398
8	2.1479	34.7845	0.0092	0.0141	0.0176
9	2.1374	38.7563	0.0219	0.0153	0.0109
10	2.1275	42.7028	0.0615	0.0532	0.0476
11	2.1183	46.6239	0.1094	0.0993	0.0922

[a] A: D_e = 337 kJ mol^{-1}, average deviation is 0.3412%; B: D_e = 346 kJ mol^{-1}, average deviation is 0.3408%; C: D_e = 354 kJ mol^{-1}, average deviation is 0.3420%.

DISCUSSION

Using the spectroscopic relation $D_e = \omega_e^2/(4\,\omega_e x_e)$, the dissociation energy D_0^o for the SnCl molecule is found to be 346 kJ mol^{-1}. Gaydon's[23] relation $D_e = \omega_e^2/(5.33\,\omega_e x_e - 2\,B_e)$ yields the D_0^o value of 270 kJ mol^{-1}. The dissociation energy estimated from the entries of Table II is $D_0^o = 343.9 \pm 8$ kJ mol^{-1}. This result agrees quite well with that suggested by Balasubramaniam[17] from a comparison with other halides belonging to the group IV A in the periodic table.

The molecular constants derived from the infrared spectra studies can be used for the estimation of dissociation energies. But the molecular constants evaluated from the electronic spectra studies are capable of giving the most accurate dissociation energies for diatomic molecules[24]. As we have used the latest and most reliable molecular constants attained from band heads measurements[16] and bearing in mind that only accurate input data will yield accurate RKR potential energy curve and also the high sensitivity of the dissociation energy derived from curve fitting method to the potential energy curve[7], we can conclude that the results can be considered satisfactory and reliable

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