Potential energy curves and dissociation energies of diatomic indium halides

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Abstract   : The RKR potential curves are computed for the ground state XO* and low-lying excited states AO* and B1 of indium monohalides using the most recent molecular constants. The H-H potential function has been shown to reproduce well the RKR curve over a wide range of energies and these potentials are applied to estimate the ground state dissociation energies(D_e") for these molecules. A brief discussion on the correlation of the low-lying excited states to the different possible dissociation products is also given.

Keywords : diatomic indium halides, RKR potentials, dissociation energies

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Knowledge of accurate potential energy curves for the different electronic states of diatomic molecules is of fundamental importance in understanding a number of molecular phenomena, e g, dissociation energies, perturbations, electronic transition moments etc. These curves form a basis for discussion of the nature of bonding in the different states of a molecule. Comparison of the experimental (RKR) potential curve with empirical potential functions has often been used with success to estimate the dissociation energy of a diatomic molecule [1-4].

The diatomic indium halides, a transient and short lived molecular species, have many attractive physical and chemical properties, such as high volatility at reasonable low temperatures, fast recombination rates and reasonably low dissociation energies. Therefore, these molecular species have received attention in both fundamental and applied research. The studies on the molecular electronic states of these molecules have been accelerated in the recent decades due to their application in the production of atomic photodissociation lasers [5,6], in the lighting industry [7], in the manufacturing of semiconductor devices including integrated circuit etc [8].

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Mainly three low-lying excited electronic states $A^3\pi_0(O^+)$, $B^3\pi_0(1)$ and $C^1\pi(1)$ of the indium monohalides are known through transitions to the ground state $X^1\Sigma^+(O^+)$ [9-23]. Of these, the $C^1\pi$ state becomes progressively less stable as the mass of the halogen increases [9]. The vibrational and rotational analyses at moderately high resolution of this group of monohalides have been reported [10-23].

An early study on the potential energy curves of IIIA group monohalides using RKR method was reported by Thakur et al [1]. Further, several group of researchers have continued their effort to construct accurate potential energy curves for the different electronic states in this group of molecules as well as for various diatomic molecules using RKR method and by other different approximation methods [1, 3, 4, 23-30].

In the present work, we have computed the RKR potentials for the XO+, AO+ and B1 states of the diatomic indium halides using the most recent vibrational and rotational constants. The computer programme used in these calculations is one developed by Tellinghuison [30]. Further Hulbert-Hirschfelder (H-H) potential is used to reproduce the RKR potentials by

varying the dissociation energy value over a wide range. This permitted us to determine the best value of dissociation energy (D_e) corresponding to maximum correlation coefficient.

(a) The diatomic indium halides are molecules with an even number of electrons and normally exist in the vapour phase. The electronic configuration for the ground state of these molecules may be written as follows .

$$..(z\sigma)^2 (y\sigma)^2 (\omega\pi)^4 (x\sigma)^2 \qquad X^1\Sigma^+ .$$
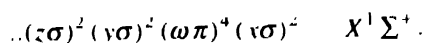
The ground state of all diatomic molecules formed by indium and other IIIA group metal atoms with halogens is a $X^1\Sigma^+$ (or O^+ in case C-type) state. The lowest excited state is $a^3\pi$ state, the coupling case again changes to Hund's case 'C' in the heavier molecules Above the A, $B^3\pi_{0,1}$ states lies the $C^1\pi$ -state. The RKR potential energy curves are calculated for the $X^1\Sigma^+$, $A^3\pi_0$, and $B^3\pi_1$, states of InX (X = ^{19}F, ^{35}Cl, ^{79}Br and ^{127}I) for the observed vibrational levels. The turning points for all the known vibrational levels have been calculated and are available with the authors (these are not included to save space). The recent values of the molecular constants and the equilibrium internuclear distance (r_e) calculated from these for the different states of InX are given in Table 1 The values of r_e increases with increasing mass of the halogen atom. The values of r_e for $A^3\pi_0$ and $B^3\pi_1$ states are slightly lower in comparison to the respective ground state value in all of these molecules. The same trend was also observed in the other IIIA group monohalides

The Hulbert-Hirschfelder potential function can be written in the following form [4].

$$U_{HH}(r) = D_e\left\{\left(1-e^{-x}\right)^2 + cx^3 e^{-2x}(1+bx)\right\},$$

where

$$x = \alpha(r - r_e), \qquad \alpha = \omega_e / 2(B_e\ D_e)^{1/2} r_e$$

$$c = 1 + a_1(D_e / a_0)^{1/2}, \qquad b = 2 - \left\{(7/12) - (D_e a_2 / a_0)\right\}/c,$$

a_0, a_1 and a_2 are the Dunham coefficients given by

$$a_0 = \omega_e^2 / 4Be, \qquad a_1 = -1 - \left(\alpha_e\,\omega_e / 6B_e^2\right),$$

$$a_2 = (5/4)a_1^2 - \left(2\omega_e x_e / 3B_e\right).$$

The above potential function is calculated, for each vibrational level of the ground state of these molecules assuming different values of the dissociation energy. The best values of D_e for the ground state of InF, InCl, InBr and InI corresponding to the maximum correlation coefficient are found to be 5.25 eV, 4.44 eV, 3.99 eV and 3.43eV, respectively. These values along with the values obtained earlier by using different methods are given in Table 2.

(b) The ground state electronic configuration of atomic Indium (In) and halogen (X) generates a ^2P term which is regular for In and is inverted for X. Although the electronic configurations and molecular states corresponding to the main electronic transitions (A, $B^3\pi_{0,1} - X^1\Sigma^+$ and $C^1\pi - X^1\Sigma^+$) in the InX have been correctly identified, the correlation of the electronic states to their dissociation products and the calculations of the ground state dissociation energy have

Table 1. Molecular constants of the $X^1\Sigma^+$, $A^3\pi_0$ and $B^3\pi_1$ States of Indium Monohalides

Molecule	Electronic states	ω_e (cm^{-1})	$\omega_e X_e$ (cm^{-1})	B_e (cm^{-1})	α_e (cm^{-1})	r_e^* (A°)	References No.
^{115}In^{19}F	$X^1\Sigma^+$	535.001	2.618	0.26214262	1.87855 ×10^{-1}	1.9861069	14
	$A^3\pi_0$	575.20	3.670	0.27320	2.0 × 10^{-3}	1.9450000	11, 33
	$B^3\pi_1$	572.20	2.630	0.27362	2.0 × 10^{-3}	1.9440000	11, 33
^{115}In^{35}Cl	$X^1\Sigma^+$	317.389	1.0316	0.1089829	5.17371 × 10^{-4}	2.4020244	12
	$A^3\pi_0$	340.040	1.880	0.1152171	6.678 × 10^{-4}	2.3332730	17, 20
	$B^3\pi_1$	339.100	2.193	0.11497	0.0	2.3386449	17
^{115}In^{79}Br	$X^1\Sigma^+$	222.930	0.5198	0.05567168	1.907596 × 10^{-4}	2.5440847	13
	$A^3\pi_0$	228.163	1.195	0.0584402	2.755 × 10^{-4}	2.4830924	21
	$B^3\pi_1$	224.328	1.2730	0.0582917	2.92 × 10^{-4}	2.4862533	21
^{115}In^{127}I	$X^1\Sigma^+$	176.8267	0.28927	0.037179	1.10465 × 10^{-4}	2.7421263	7
	$A^3\pi_0$	157.8032	1.26935	0.038363	2.17026X 10^{-4}	2.6994794	7
	$B^3\pi_1$	146.4217	2.20187	0.037858	2.8823 X 10^{-4}	2.7174244	7

* Values obtained by our calculations

Table2. Ground state dissociation energies (eV) by different procedures for the Indium monohalides.

Molecule	Thermo chemical Value (9)	Values obtained from spectroscopic methods		Best values suggested by Barrow (9)	Best values suggested by Huber and Herzberg [31]	Our value by curve fitting method
		By extrapolation on observed vibrational levels in $C^1\pi$ - state [9, 15, 23, 27]	By predissociation observed in the $C^1\pi$ - state [22, 24]			
$^{115}In^{19}F$	5.25	5.28	—	5.46	5.25	5 25
$^{115}In^{35}Cl$	4.44	4 43	4.66	4.44	4.44	4.44
$^{115}In^{79}Br$	3 99	3.91	3.71	3.99	3.99	3.99
$^{115}In^{127}I$	3 43	3 41	—	3.43	3 43	3 43

presented still some difficulty. A survey of dissociation energies of the ground and low-lying electronic states of group IIIA monohalides were reported by Barrow [9] more than four decades ago. Barrow estimated the value of the ground state dissociation energy based on the knowledge of the dissociation energies of the low-lying excited states corresponding to the different possible dissociation products. The best values of the ground state dissociation energies for InF, InCl, InBr and InI suggested by Barrow [9] and the values obtained from the other different methods are given in Table 2. According to Barrow, a high degree of ionic bonding is expected in this group of molecules. Recently, Vempati and Jones [23] have presented the correlation of dissociation products for the lowest excited states to calculate the ground state dissociation energy of InI by assuming the following two cases of chemical bond :

(i) If the ground state is considered to be a covalent one, the products, for the X-state are $In(^2P_{1/2}) + I$ $(^2P_{3/2})$, for the A-state these are In^* $(^2P_{3/2})$ + I $(^2P_{3/2})$ and for the B state, $In(^2P_{1/2}) + I$ $(^2P_{3/2})$.

(ii) If the ground state is considered to be ionic, the products for the X-state are $In^+ + I^-$, while for A and B states this will be In $(^2P_{1/2}) + I$ $(^2P_{3/2})$.

Barrow [9] has chosen case (i) as the correct description and recommended a value of ~ 3.43 eV for the dissociation energy of the ground state of InI. However, Vempati and Jones [23] have mentioned that both A and B states of InI are expected to arise from the same electronic configuration and correlated to the same dissociation products as given in the case (ii). Vempati and Jones [23] used the extending turning points of the RKR potential curves of the X, A and B states (for InI) up to the dissociation limit to estimate the dissociation energy for these states. Using the dissociation energy with the assumption of case (ii), they have obtained the most consistent value for D_e". A value of D_e"~3.41 eV obtained by assuming case (ii), in which ionic bond is suggested for the ground state of InI, was recommended by Vempati and Jones [23].

Wolf and Tiemann [25] also presented an ionic asymptote for the ground state of InCl as well as for all IIIA group

monohalides. They also indicated the value of De for the X-state of InCl which is consistent with the best value given by Huber and Herzberg [31]. Perumalsamy *et al* [24] also calculated the upper limit of dissociation energy of the X- state for InCl ~ 4.66 eV using the predissociation observed in the $C-X$ system. Singh *et al* [27] reported the value of D_e for the InBr~3.91eV by analyzing the fluctuation bands observed in the $C-X$ transition of InBr. We have also estimated the dissociation energies from

$$D_e = \frac{\omega_e^2}{4\omega_e x_e}$$ for the X, A and B states of InF, InBr and InCl to determine the most probable dissociation products for these states. It was found that extrapolated values for the dissociation energy in the ground state leads to much lower value than the best value reported earlier using other methods. This fact was taken as in agreement with the expected increasing ionic character towards lighter molecules in this group (*i.e.* InI< InBr < InCl < InF) [33,34].

The values of the ground state dissociation energy for the InX molecules calculated by our curve-fitting method, are consistent with the best values recommended by earlier workers. From the present study, we have concluded that both A and B-states of InF, InCl, and InBr, arising from the lowest excited electron configuration, are expected to correlate to the excited Indium and normal Iodine atoms, as recommended by Barrow [9]. It should also be noted that chemical bond in the indium monohalides are generally considered to be ionic [23, 25, 32]; however, the percentage of covalent bonding is slightly higher in the heavier Indium halides.

Acknowledgment

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