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TRANSITION PROBABILITIES AND DISSOCIATION ENERGY OF LaS MOLECULE

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The Frank-Condon factors (transistion probabilities) and r-centroids have been evaluated by a more reliable numerical integration procedure for the bands of $B-X$ system of LaS molecule, using a suitable potential. The dissociation energy, $D_0^0 = 480$ KJ mol^{-1} for the electronic ground state of LaS molecule has been estimated by fitting the modified Lippincott function to the experimental potential energy curve, using correlation coefficient.

1. Introduction

The knowledge of vibrational transition probabilities is required to explain the intensity distribution in a molecular band system. To a good approximation Franck-Condon(FC) factors are proportional to these transition probabilities. Accurate values of FC factors and related quantities are essential to obtain radiative life time and vibrational temperature for the astrophysical molecules.

There has been codsiderable interest in the construction of experimental potential energy curves for many diatomic molecules which are of interest in astrophysics and gas kinetics. A comparison with the experimental curves desides the empirical potential function which best fits the molecular electronic state. In particular the dissociation energy could be estimated reliably from the empirical function describing adequately the electronic ground state.

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

Lambert and Clegg [1] predict that the LaS molecule may be present in the S-type stars.

There has been no report on the FC factors and r-centroids for the $B-X$ band system of LaS molecule [2]. Therefore the reliable values of the FC factors and r-centroids for

v', v''	$\lambda_{v'v''}$ $\times 10^{-10}$m	$q_{v'v''}$	$\bar{r}_{v'v''}$ $\times 10^{-10}$m
0,0	7260.0	0.523	2.388
0,1	7507.9	0.346	2.439
1,0	7051.0	0.331	2.342
1,2	7533.2	0.325	2.444
2,1	7075.2	0.292	2.348

Tab. 1. Franck-Condon factors and r-centroids

State	ω_e $\times 10^2$m^{-1}	$\omega_e X_e$ $\times 10^2$m^{-1}	B_e $\times 10^2$m^{-1}	λ_e $\times 10^2$m^{-1}	r_e $\times 10^{-10}$m
B	410.075	0.940	0.11099	0.00034*	2.4174
X	456.700	0.965	0.11693	0.00034*	2.3552

*uncertain [2]

Tab. 2. Molecular constants

the $B^2\sum^+ - X^2\sum^+$ system of LaS have been computed by a more accurate numerical integration procedure, using the suitable potential. There has been no report on the experimental potential energy curve for LaS molecule and therefore the experimental curves have been constructed for the B and X states of LaS by the Rydberg-Klein-Rees (RKR) method. The precise value of dissociation energy for the electronic ground state of LaS molecule has also been estimated by fitting the modified Lippincott function [3] to the experimental potential energy curve, using correlation coefficient.

Marcano and Barnow [4] have analysed the $(B - X)$ band system of LaS and the vibrational and rotational constants have been reported.

2. Method

2.1. Frank Condon factors and r-centroids

The square of the overlap integral is termed as FC factor,

$$q_{v'v''} = < \Psi_{v'}, |\Psi_{v''} >^2 \tag{1}$$

where $\Psi_{v'}$ and $\Psi_{v''}$ are the vibrational wave functions for the upper and lower states respectively. The r-centroid is the unique value of internuclear separation which may be associated with a $v' - v''$ band and defined as

$$\bar{r}_{v'v''} = \frac{\langle \Psi_{v'}|r|\Psi_{v''}\rangle}{\langle \Psi_{v'}\Psi_{v''}\rangle} \tag{2}$$

The Morse [5] potential yields accurate FC factors especially for vibrational transition involving low quantum numbers [6,7]. The computation of the FC factor is made by Bates's [8] method of numerical integration according to the detailed procedure

State	v	$G(v)$ KJmol^{-1}	r_{max} $\times 10^{-10}$m	r_{min} $\times 10^{-10}$m
B	0	2.44995	2.476	2.363
	1	7.33308	2.521	2.326
	2	12.19369	2.554	2.301
X	0	2.72880	2.411	2.304
	1	8.16906	2.453	2.268
	2	13.58622	2.484	2.245

Tab. 3. Turning points for the molecular vibration in B and X states

D_e KJmol^{-1}	Correlation coefficient
472	0.9999856
482	0.9999886
492	0.9999827

Tab. 4. Dissociation energy and correlation coefficient

provided by Rajamanickam et al. [9]. Morse wave functions are calculated at intervals of 0.01×10^{-10}m for the range of r from 2.22×10^{-10}m to 2.57×10^{-10}m for every observed vibrational level of each state. Integrals in the equations (1) and (2) for the FC factors ($q_{v'v''}$) and r-centroids ($\bar{r}_{v'v''}$) are computed numerically for the bands of $B - X$ system of LaS. The results are presented in Tab. 1. The wave lengths ($\lambda_{v'v''}$) data [4] are also included. The molecular constants [2] used in the present study are listed in Tab. 2.

2.2 Experimental potential energy curve

Many methods such as Klein-Dunham-Jarmain, Rydberg-Klein-Rees, Lakshman-Rao are available to construct the experimental potential energy curve. One of the best methods of obtaining accurate potential curves is by means of Rydberg-Klein-Rees (RKR) procedure. The principle of constructing the RKR Curve is to determine the turning points $r_{max,min}$ of the molecular oscillator at each vibrational level v. The great advantage of this method is that experimentally determined energy levels form the input data.

For the experimentally known vibrational levels, the RKR method gives the turning points by

$$r_{max} = \sqrt{(f_v/g_v) + f_v^2} + f_v \tag{3}$$

$$r_{min} = \sqrt{(f_v/g_v) + f_v^2} - f_v \tag{4}$$

where f and g are calculated by the procedure of Vanderslice et al [10]. The computed values of the turning points for the molecular vibration in the B and X states of LaS are presented in Table 3.

2.3. Dissociation energy

It is possible to evaluate the dissociation energy of a diatomic molecule by fitting the empirical potential function to the experimental potential curve, using correlation

coefficient [11,12]. The procedure consists of determining the D_e - parameterised empirical potential function which best fits the experimental potential energy curve for the electronic ground state of the molecule.

The adequacy of the modified Lippincott function [3] to represent the ground state of LaS is tested using correlation coefficient. D_e is varied over a range of 382 KJ mol^{-1} to 672 KJ mol^{-1} in steps of 10 KJ mol^{-1}. The correlation coefficient is maximum when D_e = 482 KJ mol^{-1}. Only revelant results of D_e and correlation coefficient are given in Table 4. The estimated dissociation energy (D_0^0) for LaS molecule is 480 KJ mol^{-1}.

3. Results and discussion

The FC factors indicate that the (0,0) band is more intense followed by $\Delta v = \pm 1$ sequence bands. Since $r_e^{'} > r_e^{''}$, $\bar{r}_{v'v''}$ increases with increase in wavelength which is expected in the red degraded band system. The sequence difference for this system is found to be constant and is about 0.01×10^{-10}m, which suggests that the potentials are not wide. It is of interest to note that r-centroid value for (0,0) transition is slightly greater than $(r_e' + r_e'')/2$ which suggests that the potentials are not very anharmonic.

Using the relation $D_e = \omega_e^2/4\omega_e x_e$, the dissociation energy D_0^0 is found to be 646 KJ mol^{-1}. Gaydon's [13] relation $D_e = \omega_e^2/(5.33\omega_e x_e - 2B_e)$ yields the D_0^0 value as 508 KJ mol^{-1}. The estimated dissociation energy D_0^0 = 480 KJ mol^{-1} is in good agreement with this value. However, the thermochemical value is D_0^0 = 570 KJ mol^{-1}.

The difference in electronegativities of La(1.1) and S(2.5) indicates that the bonding between La and S is of covalent type. The Lippincott three parameter potential function being based on a "δ"-type model of binding is dispensably covalent in nature [14]. Hence the Lippincott potential function in the modified form is suited for LaS molecule. The molecular constants derived from the infrared spectral studies can be used for the estimation of dissociation energies, but the molecular constants derived from the electronic spectral data are capable of giving the most accurate dissociation energies for diatomic molecules [15]. The molecular constants from the electronic spectral studies have been used in the present study and therefore the result can be considered satisfactory. The force constant for the electronic ground state of LaS also indicates that the dissociation energy obtained in the present study is of correct order as compared with those for other molecules whose force constant values are nearly equal to that of LaS value.

However the present result of D_0^0 value is less than that of thermo-chemical value within the error limit of 16%. This is probably due to the uncertainly in the molecular constats [2]. Further the dissociation energy is highly sensitive to the experimental potential energy curve [12]. Therefore a serious experimental attempt must be made to improve inorder to get accurate molecular constants for the $(B - X)$ system of LaS.

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