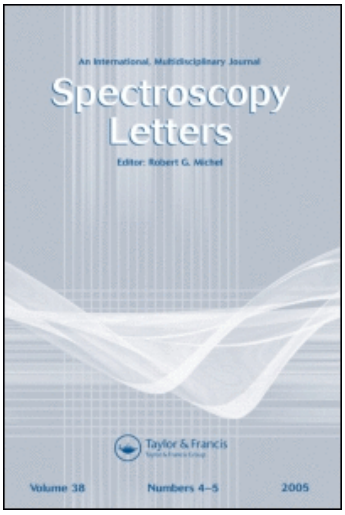

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N. Rajamanickam[a]; K. Nagarajan[b]; V. Raja[a]
[a] Physics Research Centre, V.H.N.S.N. College, Virudhunagar, India [b] P.G. Department of Physics, A.P.A. College of Arts and Culture, Palani, India

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TRANSITION PROBABILITIES AND DISSOCIATION ENERGY OF THE AsS^+ MOLECULE

N. Rajamanickam,[1]* K. Nagarajan,[2] and V. Raja[1]

[1]Physics Research Centre, V.H.N.S.N. College, Virudhunagar 626 001, India
[2]P.G. Department of Physics, A.P.A. College of Arts and Culture, Palani 624 601, India

ABSTRACT

The Franck–Condon factors and *r*-centroids, which are very closely related to relative transition probabilities, have been computed by the more reliable numerical integration procedure for the bands of the $A^1\Pi$–$X^1\Sigma^+$ system of the AsS^+ molecule, using a suitable potential. The dissociation energy for the electronic ground state of AsS^+ has been estimated by fitting the Steele and Lippincott potential function to the experimental potential energy curve, using the correlation coefficient.

Key Words: Franck–Condon factors; *r*-centroids; Dissociation energy; AsS^+ molecule

*Corresponding author. E-mail: nrvnr@india.com

INTRODUCTION

Accurate values of transition probability parameters, which are proportional to the Franck–Condon (FC) factors and *r*-centroids, are essential to evaluate all the related molecular parameters such as radiative life time, variation of electronic transition moment with internuclear separation, vibrational temperature, kinetics of energy transfer, etc.

As the stability of molecular species depends on the relative ratio of the dissociation energy and the influence of the environment, in general, it is of utmost importance for astrophysicists, chemists, and spectroscopists to determine the reliable values of dissociation energy for diatomic molecules.

To the best of our knowledge, there has been no report on the FC factors, *r*-centroids, and dissociation energy of AsS^+ molecule. Therefore, reliable values of FC factors and *r*-centroids for the bands of $A^1\Pi$–$X^1\Sigma^+$ system of AsS^+ have been computed by a more accurate numerical integration procedure, using a suitable potential. The precise value of the dissociation energy for AsS^+ has also been estimated by fitting the Steele and Lippincott (1) function to the experimental potential energy curve, using the correlation coefficient.

FRANCK–CONDON FACTORS AND *r*-CENTROIDS

Mathematically, one can write for the intensity $I_{\nu'\nu''}$ of a molecular band for a ν'–ν'' electronic transition in emission as

$$I_{\nu'\nu''} = DN_{\nu'}E^4_{\nu'\nu''}R^2_e(\bar{r}_{\nu'\nu''})q_{\nu'\nu''} \tag{1}$$

where D is a constant partially depending on the geometry of the apparatus, $N_{\nu'}$ the population of the level ν', $E_{\nu'\nu''}$ the energy quantum, $q_{\nu'\nu''}$ the FC factor, $\bar{r}_{\nu'\nu''}$ the r-centroid, and R_e the electronic transition moment. The square of the overlap integral is termed as FC factor

$$q_{\nu'\nu''} = |\langle\psi_{\nu'}|\psi_{\nu''}\rangle|^2 \tag{2}$$

where $\psi_{\nu'}$ and $\psi_{\nu''}$ 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 ν'–ν'' band and defined as

$$\bar{r}_{\nu'\nu''} = \frac{\langle\psi_{\nu'}|r|\psi_{\nu''}\rangle}{\langle\psi_{\nu'}|\psi_{\nu''}\rangle} \tag{3}$$

The Morse (2) potential yields accurate FC factors especially for vibrational transition involving low quantum numbers (3,4). The computation of FC factors is made by Bates's (5) method of numerical integration according to the detailed

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Table 1. Franck–Condon Factors and *r*-centroids

	v''							
v'	0	1	2	3	4	5	6	7
0	a) 0.029	0.106	0.191	0.223	0.193	0.131	0.073	0.034
	b) 2.010	2.033	2.056	2.080	2.103	2.126	2.148	2.171
	c) 2683.15	2730.0	2778.2	2827.8	2879.85	2931.7	2986.0	3041.5
1	a) 0.090	0.177	0.120	0.017	0.014	0.092	0.149	0.144
	b) 1.994	2.017	2.040	2.063	2.087	2.110	2.132	2.155
	c) 2652.2	2698.0	2745.1	2793.3	2843.1	2894.55	2947.8	3002.1
2	a) 0.149	0.124	0.004	0.051	0.108	0.050	*	0.042
	b) 1.979	2.001	2.024	2.048	2.071	2.094		2.139
	c) 2622.45	2667.25	–	2760.6	2809.3	2859.35		–
3	a) 0.177	0.035	0.035	0.095	0.015	0.023	0.088	0.058
	b) 1.963	1.986	2.010	2.032	2.055	2.079	2.101	2.124
	c) 2593.8	2637.7	2682.7	2728.9	2776.3	2825.3	2875.5	–
4	a) 0.167	*	0.090	0.025	0.025	0.078	0.016	0.017
	b) 1.949		1.994	2.017	2.041	2.063	2.086	2.109
	c) 2566.3		2653.3	–	–	2792.6	–	–
5	a) 0.136	0.025	0.074	0.004	0.074	0.013	0.028	0.067
	b) 1.934	1.958	1.979	2.004	2.025	2.048	2.071	2.094
	c) 2539.8	2581.9	2624.9	–	–	–	–	–
6	a) 0.098	0.067	0.024	0.047	0.037	0.015	0.062	0.004
	b) 1.920	1.943	1.964	1.988	2.010	2.034	2.056	2.079
	c) 2514.4	2555.4	2597.9	–	–	–	–	–
7	a) 0.065	0.095	*	0.070	*	0.058	0.012	0.029
	b) 1.906	1.929		1.974		2.019	2.041	2.065
	c) –	2530.1		–		–		–

a) $q_{v'v''}$; b) $\bar{r}_{v'v''}$(Å); c) $\lambda_{v'v''}$(Å); $^*q_{v'v''} = 0$.

procedure provided by Rajamanickam et al. (6). Morse wave functions are calculated at intervals of 0.01 Å for the range of r from 1.76 to 2.39 Å for every observed vibrational level of each state. Integrals in Equations (2) and (3) for the FC factors ($q_{v'v''}$) and r-centroids ($\bar{r}_{v'v''}$) are computed numerically for the bands of the A–X system of AsS$^+$ and the results are presented in Table 1. The wavelengths (7,8) data ($\lambda_{v'v''}$) are also entered. The molecular constants used in the present study are collected from the work of Shimauchi and Karasawa (8) and the compilation of Huber and Herzberg (9).

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Table 2. Dissociation Energy and Correlation Coefficient[a]

D_e (eV)	Correlation Coefficient
4.4	0.9999503
4.5	0.9999858
4.6	0.9999793

[a]These values have been calculated by using the Steele and Lippincott function.

DISSOCIATION ENERGY

In recent years, many investigators have adopted the spectroscopic method of curve fitting using correlation coefficient to estimate the reliable values of dissociation energies of diatomic molecules (10–12). The accuracy of the estimation of D_e by the curve fitting method depends on how best the empirical potential function agrees with the experimental potential energy curve.

The ground state experimental potential energy curve for AsS^+ molecule is constructed by the Rydberg–Klein–Rees (RKR) method as modified by Vanderslice et al. (13). For the constructed RKR $r_{max,min}$ values, the energies $U(r)$ are calculated with the three-parameter Steele and Lippincott function by varying the D_e value. The correlation coefficient is determined between the calculated $U(r)$ and the experimental $G(v)$ values. D_e is varied over a range of 3.5–6.5 eV. The correlation coefficient is found to be maximum when $D_e = 4.5$ eV. Only relevant values of D_e and correlation coefficients are given in Table 2. The estimated dissociation energy (D_0^0) for the AsS^+ molecule is 4.49 ± 0.13 eV. The error indicated in the result takes into account the error of 3% inherent to the Steele and Lippincott function (14).

RESULTS AND DISCUSSION

The FC factors of A–X system of AsS^+ molecule indicate that the following (0, 1), (0, 2), (0, 3), (0, 4), (0, 5), (1, 1), (1, 2), (1, 6), (1, 7), (2, 0), (2, 1), (2, 4), (3, 0), (4, 0), and (5, 0) bands are intense and all other bands are comparatively weak. The sequence difference for this system is found to be constant and is about 0.01 Å.

Using the relation $D_e = \omega_e^2/4\omega_e X_e$, the dissociation energy (D_0^0) for the AsS^+ is found to be 6.12 eV. The dissociation energies obtained with this method are often too high (11). Gaydon's (15) relation $D_e = \omega_e^2/(5.33\omega_e X_e - 2B_e)$ yields the

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(D_0^0) value as 4.75 eV. The estimated dissociation energy $D_0^0 = 4.49 \pm 0.13$ eV is in good agreement with the Gaydon's value.

The difference in electronegativities of As and S indicates that the bonding between As and S is of covalent type. The Steele and Lippincott function being based on δ-type model of binding is dispensably covalent in nature (16). Therefore, the Steele and Lippincott function is suited for AsS$^+$ molecule. The force constant also indicates that the estimated dissociation energy value of AsS$^+$ molecule is of correct magnitude.

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