

VIBRATIONAL TRANSITION PROBABILITIES AND DISSOCIATION ENERGY OF THE PF MOLECULE

Narayanan RAJAMANICKAM*, Manuel FERNANDEZ-GOMEZ**
and Juan Jesus LOPEZ-GONZALEZ

Department of Physical Chemistry,

Faculty of Experimental Sciences, University of Granada, 23071 Jaen, Spain

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The Franck-Condon factors (vibrational transition probabilities) and r -centroids have been evaluated by a more reliable numerical integration procedure for the bands of $b^1\Sigma^+ - X^3\Sigma^-$ system of the PF molecule, using a suitable potential. The dissociation energy, $D_e = 318 \text{ kJ mol}^{-1}$ for the electronic ground state of this molecule has been estimated by fitting the electronegativity function to the experimental potential energy curve.

The theoretical prediction of intensity distribution in the molecular band system requires knowledge of vibrational transition probabilities which are to a good approximation proportional to the Franck-Condon (FC) factors. A precise knowledge of FC factors and related quantities is essential for understanding and the calculation of many important data for the molecules, e.g., radiative life-times, vibrational temperature and kinetics of energy transfer.

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

There has been no report on the FC factors, r -centroids and dissociation energy for the PF molecule¹. Therefore the reliable values of FC factors and r -centroids for the bands of the $b^1\Sigma^+ - X^3\Sigma^-$ system of PF molecule have been computed by a more accurate numerical integration procedure, using the suitable potential. By fitting the electronegativity function to the experimental potential energy curve for the electronic ground

* Permanent address: Department of Physics, VHNSII College, Virudhunagar 626001, India.

**The author to whom correspondence should be addressed.

state of PF molecule, the precise value of the dissociation energy has also been estimated.

CALCULATIONS

Experimental Potential Energy Curve

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

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

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

where f_v and g_v are calculated by Vanderslice procedure². The molecular constants from Huber and Herzberg¹ used in the present study are listed in Table I. In Table II, the computed values of turning points are given for the molecular vibrations in the $b^1\Sigma^+$ and $X^3\Sigma^-$ states of PF. Morse³ potential has also been constructed and listed in Table II for a comparison. The values for Morse $r_{\max, \min}$ result from equating the vibrational energy $G(v)$ to the Morse potential energy $U(r)$ at each vibrational level. The values, in cm^{-1} , for the parameters appeared in Morse potential energy function, β and D , turn out to be, respectively, $1.7746716 \cdot 10^8$ and $41\,585.28$ for $b^1\Sigma^+$ state and $1.7705351 \cdot 10^8$ and $39\,930.14$ for $X^3\Sigma^-$ state.

TABLE I
Molecular constants for PF molecule

Parameter	State	
	$b^1\Sigma^+$	$X^3\Sigma^-$
$\omega_e \cdot 10^2, \text{m}^{-1}$	866.14	846.75
$\omega_e X_e \cdot 10^2, \text{m}^{-1}$	4.51	4.489
$\omega_e Y_e \cdot 10^2, \text{m}^{-1}$	0.0	0.019
$B_e \cdot 10^2, \text{m}^{-1}$	0.5725	0.5665
$\alpha_e \cdot 10^2, \text{m}^{-1}$	0.0045	0.00456
$r_e \cdot 10^{-10}, \text{m}$	1.581	1.589
Electronegativities	$e_1(P) = 2.1$	$e_2(F) = 4.0$

Franck-Condon Factors and r -Centroids

One of the parameters which controls the intensity distribution in the emission of molecular bands is the FC factor, which is the square of the overlap integral⁴

$$q_{v'v''} = \langle \Psi_{v'} | \Psi_{v''} \rangle^2, \quad (3)$$

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

$$\bar{r}_{v'v''} = \langle \Psi_{v'} | r | \Psi_{v''} \rangle / \langle \Psi_{v'} | \Psi_{v''} \rangle. \quad (4)$$

The Morse³ potential yields accurate FC factors especially for vibrational transitions involving low quantum numbers⁵. The computation of the FC factors are made by Bate's method⁶ of numerical integration according to the detailed procedure provided by Tawde and Murthy⁷ and Rajamanickam^{5,8-12}. Morse³ wave functions were calculated at intervals of $0.01 \cdot 10^{-10}$ m for the range of r from $1.43 \cdot 10^{-10}$ to $1.80 \cdot 10^{-10}$ for every observed vibrational level of each state. Once the appropriate wave functions are obtained, the FC factors can be evaluated by integrating the expression (3). The definition of r -centroid offers a method of computing r -centroids directly. Integrals in the Eqs (3) and (4) for the FC-factors ($q_{v'v''}$) and r -centroids ($\bar{r}_{v'v''}$) were computed nume-

TABLE II

Turning points for the molecular vibration in $b^1\Sigma^+$ and $X^3\Sigma^-$ states of PF molecule

State	v	$G(v)$ kJ mol ⁻¹	RKR		Morse	
			$r_{\max} \cdot 10^{-10}, \text{ m}$	$r_{\min} \cdot 10^{-10}, \text{ m}$	$r_{\max} \cdot 10^{-10}, \text{ m}$	$r_{\min} \cdot 10^{-10}, \text{ m}$
$b^1\Sigma^+$	0	5.1671	1.6423	1.5270	1.6416	1.5263
	1	15.4204	1.6912	1.4907	1.6901	1.4896
	2	25.5658	1.7273	1.4673	1.7259	1.4659
	3	35.6034	1.7582	1.4492	1.7564	1.4474
	4	45.5330	1.7862	1.4342	1.7840	1.4321
$X^3\Sigma^-$	0	5.0513	1.6514	1.5348	1.6503	1.5337
	1	15.0740	1.7010	1.4982	1.6995	1.4966
	2	24.9912	1.7376	1.4746	1.7357	1.4727
	3	34.8044	1.7689	1.4564	1.7667	1.4540
	4	44.5150	1.7973	1.4413	1.7947	1.4385
	5	54.1244	1.8236	1.4284	1.8208	1.4251
	6	63.6339	1.8485	1.4170	1.8455	1.4133

rically for the bands of $b^1\Sigma^+ - X^3\Sigma^-$ system of PF. The results are presented in Table III and wavelengths¹³, $\lambda_{v',v''}$ are also included.

Dissociation Energy

Curve fitting method has been found to yield reliable values for the dissociation energies of a large number of diatomic molecules^{5,14-21}. The accurate evaluation of dissociation energy by a curve fitting method requires a good empirical potential function. Szöke and Baitz²² have constructed the electronegativity potential energy function with the aid of parameters other than spectroscopic constants to link different areas in chemical physics. Therefore the electronegativity function is examined in the present study to arrive at the dissociation energy of PF molecule.

For the constructed true $r_{\max, \min}$ values, the energies $U(r)$ are calculated with the electronegativity function 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 is the value of D_e which gives the least deviation. D_e varies over a range from 145 to 485 kJ mol⁻¹ in steps of 10 kJ mol⁻¹. It is found that the electronegativity function fits the experimental curve for PF when $D_e = 318$ kJ mol⁻¹. Relevant results are given in Table IV. The dissociation energy referred to $v = 0$ level is given by $D_0^0 = D_e - G(0)$. The estimated dissociation energy for the electronic ground state of PF is 313 ± 4 kJ mol⁻¹. The error indicated in the result takes into account the error of 1.267% involved in the curve fitting.

RESULTS AND DISCUSSION

As shown in Table III, the orders of magnitude of the FC factors of all the $\Delta v = 0$ sequence suggest that they are intense. The (0,0) band is found to be relatively strong. Since $r_e < r_{e^*}$, $\bar{r}_{v',v''}$ increases with the decrease of wavelengths which is expected in a blue-degraded band system. The sequence difference for this system is found to be constant and is about $0.01 \cdot 10^{-10}$ m.

TABLE III
Franck-Condon and r -centroids for the band system $b^1\Sigma^+ - X^3\Sigma^-$ of PF

v', v''	$\lambda_{v',v''} \cdot 10^{-10}, \text{ m}$	$q_{v',v''}$	$\bar{r}_{v',v''} \cdot 10^{-10}, \text{ m}$
0, 0	7483.08	0.991	1.589
1, 1	7472.22	0.972	1.599
2, 2	7461.77	0.949	1.608
3, 3	7451.51	0.917	1.617
4, 4	7441.28	0.848	1.625

Using the relation $D_e = \omega_e^2/4 \omega_e x_e$, the dissociation energy D_0^0 is found to be 473 kJ mol⁻¹. The dissociation energies D_0^0 obtained with this method are often too high⁵. Gaydon's²³ relation $D_e = \omega_e^2/(5.33 \omega_e X_e - 2 B_e)$ yields the D_0^0 value as 371 kJ mol⁻¹. The estimated dissociation energy D_0^0 for PF molecule is 313 ± 4 kJ mol⁻¹.

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 molecules²⁴. The latest and reliable molecular constants from the electronic studies have been used in the present study and therefore the result can be considered satisfactory and reliable. Finally, the value for the harmonic force constant for the PF molecule attained from experimental frequencies, $k_e = 4.98$ mdyn Å⁻¹, indicates that the estimated dissociation energy from the electronegativity function, $D_e = 318$ kJ mol⁻¹, is of a correct order as compared with those for other similar molecules whose experimental values are known¹, e.g. NF ($k_e = 6.18$ mdyn Å⁻¹; $D_e = 344.71$ kJ mol⁻¹) and NBr ($k_e = 3.36$ mdyn Å⁻¹; $D_e = 283.94$ kJ mol⁻¹).

TABLE IV
Energy values from the electronegativity function for PF molecule for $X^3\Sigma^-$ state

v	$r_{\max, \min} \cdot 10^{-10}$ m	$G(v)$ kJ mol ⁻¹	$U(r) - G(v)$, kJ mol ⁻¹		
			$D_e = 308$	$D_e = 318$	$D_e = 328$
0	1.6514	5.0513	0.0973	0.1040	0.1106
1	1.7010	15.0740	-0.0092	0.0260	0.0599
2	1.7376	24.9912	-0.2321	-0.1555	-0.0821
3	1.7689	34.8044	-0.5403	-0.4120	-0.2893
4	1.7973	44.5150	-0.9135	-0.7246	-0.5436
5	1.8236	54.1244	-1.3651	-1.1071	-0.8597
6	1.8485	63.6339	-1.8723	-1.5369	-1.2154
0	1.5348	5.0513	-0.1380	-0.1438	-0.1491
1	1.4982	15.0740	-0.1653	-0.1942	-0.2217
2	1.4746	24.9912	-0.1421	-0.2022	-0.2596
3	1.4564	34.8044	-0.1252	-0.2216	-0.3137
4	1.4413	44.5150	-0.1242	-0.2606	-0.3906
5	1.4284	54.1244	-0.1804	-0.3591	-0.5296
6	1.4170	63.6339	-0.2676	-0.4905	-0.7032
Average deviation, %			1.270	1.265	1.271

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