

POTENTIAL ENERGY CURVES AND DISSOCIATION ENERGY OF THE PO MOLECULE

C. V. V. S. N. K. SANTHARAM AND P. TIRUVENGANNA RAO

SPECTROSCOPIC LABORATORIES, DEPARTMENT OF PHYSICS, ANDHRA UNIVERSITY
WALTAIR

(Received March 6, 1962)

ABSTRACT. From the observed head-head separations of the $C'-X^2\Pi$ system of PO reported by the authors (1962), approximate values of B_0' and τ_0' of the C' state have been estimated. Potential energy curves have been drawn for the X , B and C' levels of PO . Probable dissociation products of these states have been discussed. The dissociation energy of PO molecule is estimated as 6.8 e.v.

A study of the spectrum of the PO molecule by the authors (1962) excited in a high frequency discharge has led to the analysis and identification of two new doublet systems of bands in the ultraviolet region designated as $C'-X^2\Pi$ and $B'-X^2\Pi$. The bands of the $C'-X$ system were observed to be double double-headed and were accordingly ascribed to the transition $^2\Sigma$ (or $^2\Delta$)- $^2\Pi$. Neglecting what are likely to be small effects arising from Λ -type doubling, spin splitting and the influence of D terms, approximate B values for the vibrational levels of the upper C' state can be obtained from head-head separations. Treatment of the branch formulae gives

$$(R_{21})_{head} - (R_1)_{head} = \frac{2B'_1 B_1''}{B_1'' - B'_1}$$

$$(R_2)_{head} - (Q_2)_{head} = \frac{2B'_2 B_2''}{B_2'' - B'_2} \quad \dots (1)$$

where B_1'' and B_2'' are the effective B -values for the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ sub-levels, and

$$B_1'' = B_0''(1 - B_0''/A), \quad B_2'' = B_0''(1 + B_0''/A) \quad \dots (2)$$

and B_0'' is the true value. Using the true B_0'' values of the ground state $X^2\Pi$ and A the coupling constant obtained by Suryanarayana Rao (1958) from the rotational analysis of the γ system, the effective B_1'' and B_2'' values are calculated according to relations (2). The head-head separations in the intense (0, 1), (0, 2), (0, 3), (0, 4) sub-bands and the derived values of B_0' according to relation (1) are shown in Table I.

TABLE I

The head-head separations in the (0, 1), (0, 2), (0, 3), (0, 4) sub-bands and the derived values of B_0'

v', v''	$B_2 - Q_2$	B_0'	$B_{21} - R_1$	B_0'
0,1	10.4	0.638	11.9	0.644
0,2	11.2	0.639	10.8	0.633
0,3	12.7	0.643	13.4	0.643
0,4	13.3	0.642	13.3	0.638

From these an approximate value of B_0' was estimated as 0.64 cm^{-1} . The value of r_0' was then obtained as 1.58 \AA from the relation $r_0' = \frac{4.1061}{\sqrt{\mu_A B_0}} \times 10^{-8}$ (Herzberg page 180).

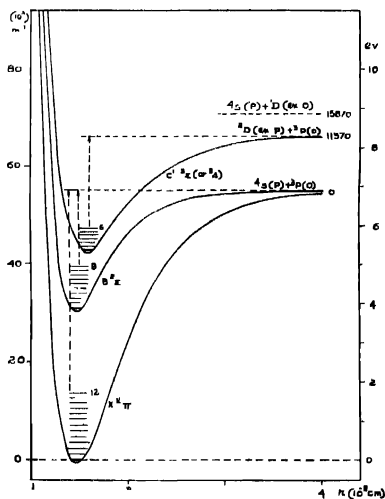


Fig. 1. Potential curves of the X, B and C' electronic states of the PO molecule.

Using the vibrational and rotational constants of the X, B and C' states, potential energy curves have been drawn adopting the Morse relation $U(r) = E_0 + D_0(1 - e^{-\beta(r-r_0)})^2$. These curves for the X $^2\Pi$ ground state and the excited B $^2\Sigma$ (the upper state of the β system) and C' $^2\Sigma$ (or $^2\Delta$) states are shown in Fig. 1. For the C' state the value of r_0 ($\approx r_e$) is used in drawing the potential energy curve. The probable dissociation products are given on the right in Fig. 1.

A linear extrapolation of the vibrational levels of the ground state X gives a value 57000 cm^{-1} (7.1 e.v.) for the dissociation energy of the PO molecule. The vibrational analysis of the β system by K. Dressler (1955) shows that the vibrational levels of the B state converge very rapidly and therefore allow a reliable estimation of this dissociation energy. The linear extrapolation of the vibrational energy levels of the B state gives $D'_0 = 24000 \text{ cm}^{-1}$. Thus the convergence limit of the bands of the $B-X$ system is $30806 - 24000 = 54806 \text{ cm}^{-1}$ or approximately 55000 cm^{-1} , above the $v'' = 0$ of $X^2\Pi_1$ level.

A similar extrapolation of the vibrational levels of the C' excited state, whose spacings decrease uniformly, gives a value for D'_0 equal to $25,200 \text{ cm}^{-1}$. The convergence limit of the bands of the $C'-X$ system is $43650 - 25200 = 68850 \text{ cm}^{-1}$, above the $v'' = 0$ of $X^2\Pi_1$ level.

We may now discuss the probable dissociation products of the X , B , and C' states. The P atom has three low lying states 4S ground state and the two 3D , 3P metastable states. The oxygen atom has three low lying states. The 3P ground state and the metastable 1D and 1S states. The X ground state may be expected to dissociate into two normal atoms $^4S(P) + ^3P(O)$. This lowest combination ($^1S_u + ^3P_g$), according to Wigner and Witmer's rules, gives rise to one Σ^+ and one Π state with each of the multiplicities 2 and 4. The $^2\Pi$ state belonging to this combination can be correlated unambiguously with the observed $X^2\Pi_1$ ground state of PO . Assuming the validity of noncrossing rule, the $^2\Sigma$ state can be correlated with the observed first excited $B^2\Sigma$ state which has been established by Nandalal Singh (1959) from a detailed rotational analysis. Thus both the B and X states dissociate into two normal atoms. The second excited $A^2\Sigma^+$ state of PO may be assumed to dissociate into an excited P atom in a $4s$ orbit and unexcited $^3P(0)$ similar to the upper state of the γ system of NO .

From the observed convergence limit of 55000 cm^{-1} of the vibrational levels of the B state, we may therefore estimate the dissociation energy of the PO molecule as 55000 cm^{-1} (6.8 e.v.) which may be higher than the true value by an amount of about 0.1 e.v. The linear extrapolated value of the ground state vibrational energy levels is 57000 cm^{-1} . The fact that this is 5 per cent higher than the above value can reasonably be attributed to the uncertainty in the extrapolated value of the ground state.

The convergence limit of the C' state was obtained as 68850 cm^{-1} . The difference between the convergence limits of C' and B states is equal to 14000 cm^{-1} . This corresponds either to the excitation energy 11370 cm^{-1} of 3D state over the 4S state of the P atom or the excitation energy $15,870 \text{ cm}^{-1}$ of 1D above the 3P ground state of O atom. Thus the C' state may dissociate into either 3D (excited P) + 3P (unexcited O) or 4S (unexcited P) + 1D (excited O). As the linear extrapolated value D'_0 of the C' state will in general be higher than the true value, the true convergence limit of the C' state would be less than 68850 . So the difference

between the convergence limits of the C' and B states is expected to be less than 14000 cm^{-1} . Hence the C' state may not possibly dissociate into 4S (unexcited P)+ 1D (excited 0). Further the C' state which should arise from a $^2\Sigma$ or $^2\Delta$ term cannot result from this combination. It may be reasonable to conclude that the C' state dissociates into a 2D (excited P)+ 3P (unexcited 0). This combination gives rise to $\Sigma^+(2)$, Σ^- , $\Pi(3)$, $\Delta(2)$ and ϕ states with each of multiplicities 2 and 4. The C' state may therefore be identified as a $^2\Sigma$ (or $^2\Delta$) state of this combination. The difference between 14000 cm^{-1} and 11370 cm^{-1} can reasonably be attributed to the uncertainty in the linear extrapolated value of D'_0 of the C' state.

ACKNOWLEDGMENT

The authors wish to express their thanks to Prof. K. R. Rao for his kind interest in this work. One of the authors (C. V. V. S. N. K. Santharam) is grateful to the C.S.I.R. (Delhi) for the award of a Research Fellowship.

REFERENCES

- Dressler, K., 1955, *Helv. Phys. Acta*, **28**, 563-690.
Nandalal Singh, 1959, *Can. Jour. Phys.*, **57**, 136.
Santharam, C. V. V. S. N. K. and Rao, P. T., 1962, *Z. Physik* **168**, 553.
Suryanarayana Rao, K., 1958, *Can. J. Phys.*, **36**, 1526.