

POTENTIAL ENERGY CURVES AND DISSOCIATION ENERGIES OF SOME DIATOMIC MOLECULES

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ABSTRACT. The potential energy curves have been constructed for the 3 known states of VO, using Lippincott's as well as Morse's potential function. The comparison of the most probable transitions predicted from the two sets of curves with the available intensity data for the yellow-green and the infra-red systems of VO reveal Lippincott's function to be closer to the true potential function. The function has further been used to calculate the dissociation energies of some diatomic molecules.

POTENTIAL ENERGY CURVES

Though Morse's (1929) expression for the potential energy of a molecule is, by far, the most commonly employed, the one developed by Lippincott (1953), viz.,

$$V = D_e(1 - e^{-n(\Delta r)^2/2r}) \quad \dots (1)$$

promises to be valuable (Lippincott 1953; Laud 1962). A good potential energy function, besides satisfying the requisite criteria at extreme limits, viz. at $r \rightarrow 0$, $r = r_e$ and $r \rightarrow \infty$, must not be away from actual curve in the intermediate positions. The intermediate behaviour of a function may be judged by a comparative study of the most probable transitions obtained from the curves on the basis of the Franck-Condon principle and those lying on the Condon parabola obtained experimentally. In the present note, the quantitative intensity data on the Yellow-green system of VO, obtained by the present authors and those on the infra-red system of the same molecule obtained by Keenan and Schroeder (1952), have been brought to bear on the graphical results obtained from Lippincott's expression with a view to examine the function from this point of view.

The potential energy curves have been constructed for the three states of VO, viz., the ground state, the upper state of the infra-red system, and the upper state of the well-known yellow-green system. The values of the constants w_e , $w_e x_e$ and r_e corresponding to the lower and the upper states of the yellow-green system have been given by Lagerqvist and Selin (1957); w_e and $w_e x_e$ for the upper state of the infra-red system were obtained by Keenan and Schroeder (1952). However, r_e for this state was not available in the literature. This was obtained by using the relation $w_e r_e^3 = \text{constant}$ which, for the different electronic states of the same molecule, is found to hold fairly well. The values of the constant for

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the lower and the upper states of the yellow-green system obtained from this relations are :

Lower state : 4058.48, Upper state : 4047.40

Using the mean value of these i.e. 4052.94 as the value of the constant, r_e for the upper state of the infra-red system comes out to be 1.650\AA . Using this value of r_e and the other relevant constants, presented in table I, potential energy curves have been constructed for the three states of VO molecule (fig. 1). We have also constructed potential energy curves for the same three states using Morse function for a comparative study (fig. 2).

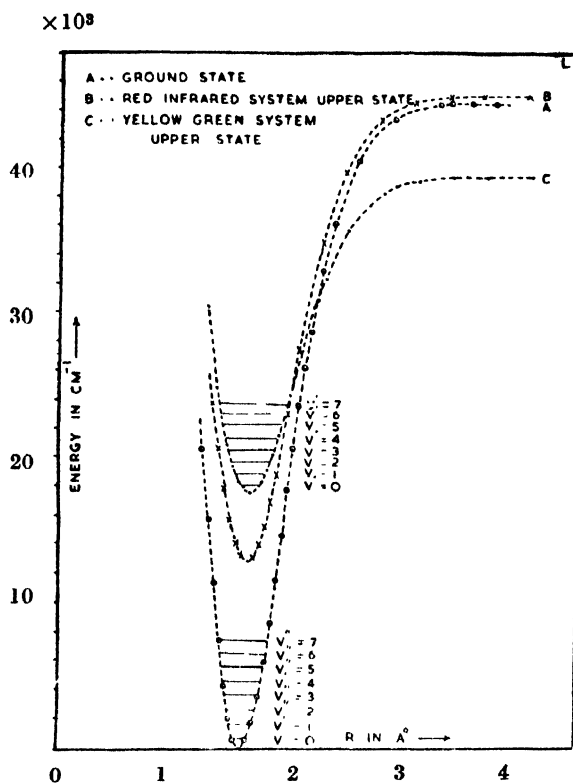


Fig. 1. Potential energy curves (Lippincott function)

Table I
 Constants

| State | w_e | $w_e x_e$ | | Author |
|-----------------------------|---------|-----------|--------|-------------------------------|
| Lower | 1011.56 | 4.97 | 1.589 | Lagerqvist and Selin, (1957). |
| Upper (Infra-red system) | 908.2 | 5.0 | 1.650* | Keenan and Schroeder, (1952). |
| Upper (Yellow-green system) | 865.9 | 6.6 | 1.672 | Lagerqvist and Selin, (1957). |

* This value was obtained by the procedure explained above.

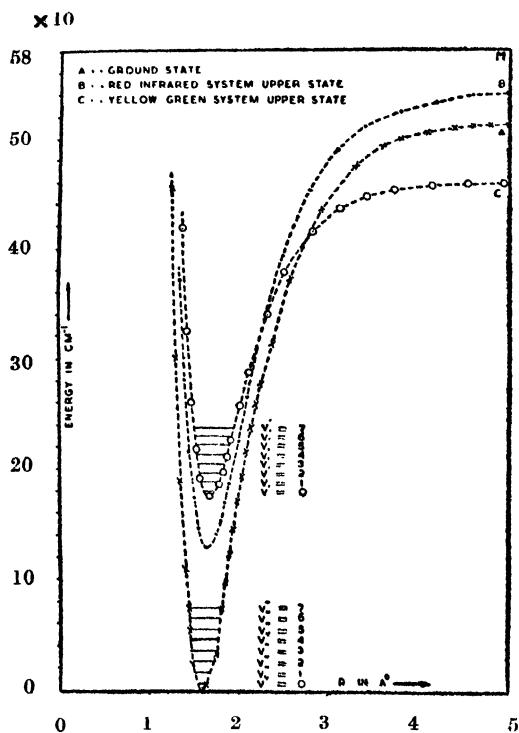


Fig. 2. Potential energy curves (Morse function)

In table 2, we give some of the most probable transitions of the yellow-green system predicted from the two sets of curves and those obtained by the present authors in the spectral study of VO molecule. In table 3, we present similar sets of values for the infra-red system of VO, the experimental values given there being those of Keenan and Schroeder (1952).

Table 2
Some of the most probable transitions : Yellow-green system

| Experimental | Lippincott | Morse |
|--------------|------------|-------|
| (0,0) | (0,0) | (0,0) |
| (1,0) | (1,0) | (1,0) |
| (2,2) | (2,1) | (2,0) |
| (3,2) | (3,2) | (3,0) |
| (4,4) | (4,4) | (4,1) |
| (5,5) | (5,5) | (5,1) |
| (6,5) | (6,5) | (6,2) |

Table 3

Some of the most probable transitions, Infra-red system

| Experimental | Lippincott | Morse |
|--------------|------------|-------|
| (0,0) | (0,0) | (0,0) |
| (0,1) | (0,1) | (0,2) |
| (1,0) | (1,0) | (1,0) |
| (1,2) | (1,2) | (1,3) |
| (2,0) | (2,0) | (2,0) |
| (3,1) | (3,1) | (3,0) |
| (5,3) | (5,3) | (5,1) |

The tables reveal clearly that the Lippincott's expression gives a better fit with experimental values than Morse's. Hence, we have enough justification to assume Lippincott's function to be closer to the true potential function.

DISSOCIATION ENERGIES

There have been some controversies about the dissociation energies of VO, TiO and ZrO.

Mahanti (1935) has found the value 6.3 e.v. for the dissociation energy of VO by linear extrapolation analytically. Herzberg (1950) supports this value; while Gaydon (1947) favours 5.5 ± 1 e.v., obtained by graphical extrapolation.

Christy (1929) has given 6.9 e.v. as the dissociation energy of TiO. Gaydon (1947) favours 5.5 ± 1 e.v. Recently Brewer (1953) has found the value to be 6.94 e.v.

For ZrO, the values suggested so far are : (1) 7.8 e.v. (Herzberg, 1950) and 6.5 ± 1.5 e.v. (Gaydon, 1947).

A correct estimate of dissociation energy can be made if the exact molecular potential is known. As has been indicated above, Lippincott's function is in all respects closer to the true potential function. Using this function in Schrodinger equation, the following relation is obtained.

$$D_e(\text{ergs/molecule}) = \frac{K_e}{(64\pi^2 c \mu \omega_e x_e / 3h) - 1/r_e^2} \quad \dots (2)$$

We used this relation to compute the dissociation energies of VO, TiO and ZrO, constants used being those given by Lagerqvist and Selin (1957) for VO and Lowater (1929; 1932) for the other two molecules. The dissociation energies

thus found are given in table 4 along with those obtained from the similar relation arising from Morse function, viz. $D_e = w_e^2/4w_e x_e$.

Table 4
Dissociation energies in e.v.

| Molecule | Lippincott | Morse |
|----------|------------|-------|
| VO | 4.99 | 6.38 |
| TiO | 5.35 | 6.83 |
| ZrO | 6.18 | 7.78 |

It will be observed that the values obtained by using Lippincott's expression are about 21% less than those obtained from Morse function and are closer to those estimated by Gaydon. However, for VO and TiO, Gaydon has suggested the same value, viz. 5.5 e.v., while, the one calculated above for VO is lower than that for TiO. It may be mentioned here that Merrill (1940), from his study of astrophysical data, observed that the dissociation energy of VO should be less than that of TiO. The above results conform to this conclusion.

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