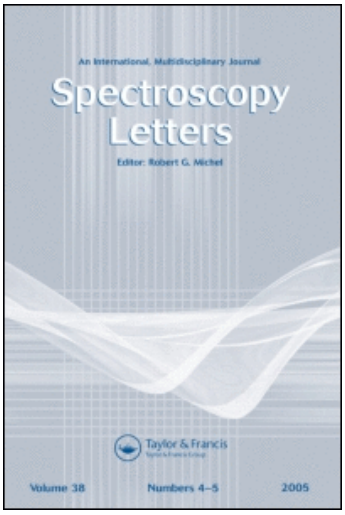

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Dissociation Energy of AsCl

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DISSOCIATION ENERGY OF AsCl

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The preferential excitation of AsO in a chemiluminescent reaction of $AsCl_3 + O_2 + K$ has been discussed. On the basis of the observed v' = 2 level of AsO in the energy state $A^2\Sigma$ the dissociation energy of AsCl has been estimated and was found to be 86.8 K Cal/mole.

The diatomic molecule AsCl has not been known spectroscopically, its dissociation energy has not been determined accurately. Gaydon (1) has given the dissociation energies of NCl, SbCl, and BiCl as 92 ± 11.5, 85 ± 11.5 and 72.3 ± 2.3 K Cal/mole respectively. If one plots the dissociation energies (disregarding the uncertainties reported by Gaydon (1)) of these molecules against the number of electrons in the respective molecules, one obtains a smooth curve from which one can estimate the average value of the dissociation energy of AsCl as 89.1 K Cal/mole.

It is interesting to note that Kushawaha et al.(2) have excited a number of bands belonging to the A'-X and A"-X system of AsO in a low pressure diffusion flame of $AsCl_3 + O_2 + K$. But they could observe, only v' = 0, 1, and 2 bands of the $A^2\Sigma - X^2\Sigma$ system

of AsO in addition to some potassium doublets. The excitation mechanism of these doublets is reported in an other communi cation (3). Among the various reactions responsible for the excitation of AsO upto v' = 2 level of the $A^2\Sigma$ state, the following seems to be one of the best candidates:

$$AsCl + KO \longrightarrow AsO^* + KCl \qquad \ldots (1)$$

It will further be noted that AsCl can be readily produced during the following reactions :

$$K\,(4^2P) \longrightarrow K\,(4^2S) + h\nu \quad (37.1\ KCal) \qquad \ldots (2)$$

$$AsCl + h\nu\ (37.1\ KCal) \longrightarrow AsCl\ (37.1\ KCal) \qquad \ldots (3)$$

$$K\,(4^2P) + AsCl \longrightarrow AsCl\ (37.1\ KCal) + K\,(4^2S) \qquad \ldots (4)$$

Kushawaha et al. (2) have observed several transitions in potassium from the upper ^2P and ^2S states to the lower 4^2P state which indicate that this 4^2P state got well populated. In view of the fact that the life time of this state is very small (2.8×10^{-8} sec) transitions from this to the ground state will be more frequent and will give rise to photons of energy 37.1 K Cal. These photons could be absorbed by AsCl and send the molecule to an appropriate higher vibrationally excited state as shown in equations (2,3). Thus equation (1) can be rewritten as :

$$AsCl + KO \longrightarrow AsO + KCl + (\triangle H + 37.1\ K\ Cal) \qquad \ldots (5)$$

If it is assumed that the available energy of this reaction ($\triangle H$ + 37.1 K Cal) is all be taken up by AsO where by this molecule goes to the v' = 2 level in the upper state A (as observed by

Kushawaha et al. (2)), one can then readily calculates the dissociation energy of AsCl as follows :

$$D_o\ (AsO) + D_o\ (KCl) - \left[D_o(AsCl) - 37.1\ KCal\right] - D_o(KO)$$
$$= \text{energy corresponding to } v' = 2$$
$$\text{to } v'' = 0 \text{ transition in the A-X system of AsO.}$$
$$\ldots (6)$$

Substituting D_o (AsO) = 113 KCal, D_o (KCl) = 100.5 KCal from ref.(1) and D_o (KO) = 70 KCal from ref.(4), and the energy corresponding to v' = 2 to v" = 0 transition in AsO (32822.0 cm^{-1} = 93.8 KCal), one obtains the dissociation energy D_o for AsCl equal to 86.8 KCal This value matches well with the predicted value of 89.1 KCal.

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REFERENCES

A.G. Gaydon, "Dissociation Energy and spectra of diatomic molecules", Chapman and Hall Ltd. London (3rd Edition), 1968.

2. V.S. Kushawaha, B.P., Asthana, and C.M. Pathak J. Mol. Spectrosc. 41, 577, 1972.

3. V.S. Kushawaha, B.P. Asthana, and C.M. Pathak
J. Chem. Phys. (accepted).

4. JANAF Thermochemical Table, U.S. Govt. Printing Office, Washington, D.C. 1965.

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