NOTE

ON THE OSCILLATOR STRENGTHS OF MgO AND F_2

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Abstract—In a recent paper (R. P. MAIN, D. J. CARLSON and R. A. DuPUIS, *JQSRT* 7, 805 (1967)), measurements of oscillator strengths of electronic transitions in the MgO-, MgH-, and F_2-molecules were reported. We point out that the results reported in that paper for F_2 are almost certainly invalid, and that an error in the oscillator strengths for the MgO transitions, estimated in that paper and due to the possible existence of low-lying electronic states of MgO, was incorrectly calculated. ·

IN A RECENT paper,[1] measurements in emission of oscillator strengths of electronic transitions in the MgO-, MgH-, and F_2-molecules were reported. The authors stated that their results for MgO might be too small by as much as a factor of four if certain predicted low-lying electronic states of this molecule actually existed. This error was estimated considering only the effect of these low-lying electronic states on the electronic partition function of MgO, and therefore on the computed number density of MgO-molecules. This error is reduced in this case if one correctly considers this problem, for the electronic partition function also partly determines the relative population of the emitting excited state ($B^1\Sigma^+$) of MgO.

The procedure that should have been applied in estimating this error employs formulae that have been given in the literature by one of us.[2] When the effect of the possible error in the electronic partition function of MgO on the population of the MgO $B^1\Sigma^+$ electronic state is correctly computed for the case presented in Ref. 1, it is found that the oscillator strengths for the MgO ($B^1\Sigma^+-X^1\Sigma^+$) and ($B^1\Sigma^+-A^1\Pi$) band systems reported in Ref. 1 will be only about 30 per cent too small if the predicted low-lying electronic states of MgO actually exist.

Two recent papers[3,4] on the spectrum of F_2 have contributed to our knowledge of this molecule, but make questionable the determinations of the scaled transition probabilities of the bands at 5731 Å and 5394 Å observed in the work of Ref. 1. PORTER[3] has assigned the F_2 5731 Å band to a ($^1\Sigma_u^+-^1\Pi_g$) transition, while STRICKER and KRAUSS[4] identify this band as belonging to a ($^1\Pi_g-^1\Sigma_u^+$) transition. Both agree that this band is a (0, 3) band, and Stricker and Krauss inferred from vacuum ultraviolet absorption studies that the upper electronic state of this transition, which they call $D^1\Pi_g$, has a T_0-value of 126,370·5 cm^{-1}. Porter has found no 5394 Å band, but rather two bands of his ($C^1\Sigma_u^+-B^1\Pi_g$) system that fall very near to 5394 Å, while Stricker and Krauss state that the 5394 Å band belongs to a second ($^1\Pi_g-^1\Sigma_u^+$) system, which has an upper electronic state different from that of the system to which the 5731 Å band belongs, but which has the same lower electronic

state. This upper state has a T_0-value nearly equal to that of the $D^1\Pi_g$-state according to Stricker and Krauss.

If we use these T_0-values to transform the scaled transition probabilities of Ref. 1, ignoring the disagreements of Porter and Stricker and Krauss, we obtain results that are absurdly large. It would appear, then, that either the scaled transition probabilities of Ref. 1 or the inferred T_0-values of Stricker and Krauss are in error. The latter possibility seems very unlikely; the T_0-values of Stricker and Krauss would have to be reduced by an amount of about $80\,000\,\text{cm}^{-1}$ for Ref. 1 to be vindicated, and this would mean that there must exist further visible bands of F_2 which have never been observed. Furthermore, lowering the T_0-values of Stricker and Krauss by this amount would mean that the excited electronic states they found cannot correlate with the possible dissociation products of F_2 without postulation of very large (about 8 to 13 ev) dissociation energies for all but for one of the $^1\Pi_g$-states which might correlate with ground state F-atoms through a large maximum in its rotationless potential energy curve. This situation does not seem likely, and it appears certain that the identification in Ref. 1 of the $5731\,\text{Å}$ and $5394\,\text{Å}$ bands observed there as being due to F_2 is erroneous. Thus, it is recommended that the transition probabilities quoted there be disregarded.

Dr. W. Stricker has mentioned to us the considerable nitrogen content of commercial fluorine gas; it could be that in the experiments of Ref. 1 there exist emissions due to NF, NF_2, NF_3, NH, NH_2, NH_3, NO, N_2, etc. It seems that some of the observed band structures, including those at $5731\,\text{Å}$ and $5394\,\text{Å}$, can be correlated with the known spectra[5] of NH_2, NO_2, and N_2, but we cannot make certain identifications here. This points up a difficulty connected with optical studies of thermochemically complex systems.

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