The Emission and Fluorescence Spectra of Sulphur Dioxide

In a paper in this issue, Chow has discussed the emission and absorption spectra of SO_2. In the *Zeitschrift für Physik*[1] which came to our laboratory just after Chow's paper was sent in, Lotmar has presented his results on the fluorescence spectrum in the same region.

Lotmar's fluorescence was excited by the Zn line at 2100A (47,600 cm^{-1}) which falls on the SO_2 absorption band having its violet edge at 47,623 according to Chow. This corresponds to excitation to the B_2 level in Chow's scheme of analysis. Since only part of any band will appear in fluorescence there may be a considerable interval between the center of the fluorescence band which is measured by Lotmar and the violet edge of the same band measured by Chow in emission. Furthermore this interval may vary for different bands, especially for different types of vibrational transition. Consequently a direct comparison of the wave numbers in Chow's list and Lotmar's list has little point. However, comparing the 47,600 value given by Lotmar for the fluorescence band corresponding to the 47,623 (or 47,631 in emission) band of Chow, we may guess that Lotmar's wave numbers should run about 25 cm^{-1} below Chow's.

Making this correction I have compared Lotmar's series with Chow's data in detail and find a fair agreement. Of the three 1370 (ν_3 of Chow, ν_1 of Lotmar) progressions reported by Lotmar (α, β, γ-series) none had been reported completely by Chow, but the first two and fifth and sixth of the α-series and the first two of the γ-series are in his list. The β-series is not.

Of the 1150 (ν_1 of Chow, ν_2 of Lotmar) progressions, the *A*, *B* and *C* series are almost completely represented by bands in Chow's list but by bands usually fitting better elsewhere in his analysis. The *D*, *E*, *F* and *G* series receive no support from Chow's work.

Of the 520 (ν_2 of Chow, ν_3 of Lotmar) progressions, most of the *a*-series has already been recorded by Chow, while the *c*-series has many agreements in spite of four gaps in the list of thirteen bands. The *b*, *d*, *e*, *f* and *g* series receive little or no confirmation but the six members of the *h*-series all appear in Chow's list.

A more significant and more striking comparison is that between the numerical values for the vibrational levels in the normal state as derived from Chow's and from Lotmar's data. They are given in Table I.

TABLE I. *Vibration levels in* SO_2. $\nu_1=1150$; $\nu_2=520$; $\nu_3=1370$.

Level	Chow	Lotmar	Level	Chow	Lotmar
$1\nu_1$	1150	1150	$1\nu_2$	521	520
$2\nu_1$	2300	2300	$2\nu_2$	1043	1040
$3\nu_1$	3450	3450	$3\nu_2$	1553	1560
$4\nu_1$	4600	4600	$4\nu_2$	2069	2075
$5\nu_1$		5750	$5\nu_2$	2578	2590
$6\nu_1$		6900	$6\nu_2$	3086	3110
		etc.	$7\nu_2$	3590	3630
			$8\nu_2$	4093	
				etc.	
$1\nu_3$	1354?	1370	$\nu_1+\nu_2$	1670	1670
$2\nu_3$	2676?	2720	$\nu_1+2\nu_2$	2205	2180
$3\nu_3$	3966?	4060	$\nu_1+\nu_3$	2502	2505
$4\nu_3$		5385			
		etc.			

It is clear that the only serious discrepancy is in the ν_3 progression where Chow's values were admittedly tentative. I think the long progressions of ν_1 and ν_2 with very slow convergence are well established, particularly the ν_2. The ν_3 progression depends almost entirely on Lotmar's work, with some confirmation in the α-series. Perhaps the most interesting agreement is the $\nu_1+\nu_3$ level. This level came out of Chow's analysis purely empirically yet is found to agree perfectly with Lotmar's result and with the infrared value of 2499.[2] As Lotmar points out coupling between these two vibrations is reasonable and I think we may say that we know its amount quite accurately for this first combination.

H. D. SMYTH

Palmer Physical Laboratory,
Princeton, N. J.,
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[1] Lotmar, Zeits. f. Physik **83**, 765, 785 (1933).
[2] Dadieu and Kohlrausch, Phys. Zeits. **33**, 167 (1932).

The Isotopes of Hydrogen by the Magneto-Optic Method. The Existence of H^3

In order to test further the presumption that the minima observed in the magneto-optic method as developed by Allison[1] depend upon the isotopes of the positive ions present, we examined water solutions containing approximately 2 and 4 percent of heavy hydrogen (H^2). A solution of HCl in ordinary water gives minima at 15.74 and 15.85 (Allison units); the latter, which is presumably due to H^1, is considerably stronger. These values agree with those reported by Allison in his earlier work in which he concluded the existence of H^2. In the heavy water solution we find the intensity of the 15.74 minimum almost equal to the one at 15.85 and in addition a third minimum at 15.65. The position of this minimum corresponds to that expected of H^3, and its intensity is somewhat less than the 15.74 minimum (H^2) in ordinary water.

We have checked the HCl results with HBr. The minima in the solution in ordinary water are at 12.97 and 13.09 and the new minimum in the heavy water solutions is at 12.84.

The heavy water was supplied to us by Professor G. N. Lewis, and he and Dr. Spedding are carrying out further spectroscopic investigations of the existence of H^3.

WENDELL M. LATIMER
HERBERT A. YOUNG

Department of Chemistry, University of California,
Berkeley, California,
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[1] Allison and Murphy, J. A. C. S. **52**, 3796 (1930). Allison, Ind. Eng. Chem. Anal. Ed. **4**, 9 (1932). See Phys. Rev. **37**, 1178 (1931) for halogen acid values.