

## A Transition in Potassium Superoxide

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TABLE I. Observed and calculated Raman frequencies of  $D_2$ .

$\nu$	$J$	$\nu$ obs. $\text{cm}^{-1}$	$\nu$ calc. $\text{cm}^{-1}$	Difference	$I$ calc.
0-0	0-2	$179.6 \pm 0.5$	179.1	0.5	
	1-3	$298.3 \pm 1.3$	297.4	0.9	
0-1	0-0	$2989.5 \pm 1.3$	2996.7	-7.2	0.00*
	1-1		2994.7	-5.2	0.90
	2-2		2991.2	-1.7	1.21
	3-3		2986.2	3.3	0.33
	4-4		2974.7	14.8	0.26,

means in measuring plates are given in Table I, together with frequencies calculated from the equation of Urey and Teal, for the rotation-vibration energy levels of the molecule in the ground state. Using a formula given by Placzek<sup>5</sup> and due to Mannenbeck, we have calculated the relative intensities  $I$  of four of the strongest lines in the vibrational  $Q$  branch. The result gives  $2990.0 \text{ cm}^{-1}$  for the position of the center of gravity of the  $Q$  branch, and this is in agreement with the observed frequency.

The constants of Urey and Teal are therefore confirmed. This result is important in connection with the use of deuterium to establish the structure of hydrogen-containing molecules.<sup>6</sup> In such cases  $M-D$  distances are assumed equal to  $M-H$  distances, where  $M$  is any atom. The greatest deviation from this assumption would probably occur in  $D_2$ ; and since no deviation is found in this case the assumption appears to be justified. Moreover the force constant for  $D_2$  is the same as that for  $H_2$ , and this suggests that  $M-D$  force constants are equal to those for  $M-H$ .

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March 2, 1935.

<sup>1</sup> M. F. Ashley, Phys. Rev. **43**, 770 (1930); G. H. Dieke and R. W. Blue, Nature **133**, 611 (1934); Phys. Rev. **47**, 261 (1935).

<sup>2</sup> C. R. Jeppesen, Phys. Rev. **45**, 480 (1934); **44**, 165 (1933).

<sup>3</sup> H. Beutler and K. Mie, Naturwiss. **22**, 418 (1934); K. Mie, Zeits. f. Physik **91**, 475 (1934); H. Beutler, Zeits. f. physik. Chemie **B27**, 287 (1934).

<sup>4</sup> H. C. Urey and G. K. Teal, Rev. Mod. Phys. **7**, 34, (1935). Table XV, p. 80. A complete set of references is given in this review.

<sup>5</sup> G. Placzek, *Rayleigh-Streuung und Raman-Effekt* (Leipzig, 1934) Eqs. (15), (15a), p. 343.

<sup>6</sup> F. Rasetti reports a value  $\nu_{10}^0$  for hydrogen. Phys. Rev. **34**, 367, (1929). The matter is worth further investigation.

<sup>7</sup> For example the structure of  $NH_3$ : Barnes, Benedict and Lewis, Phys. Rev. **45**, 347 (1934).

### A Transition in Potassium Superoxide

During the study of the magnetic properties<sup>1</sup> of potassium superoxide,  $KO_2$ , I noticed that on cooling in liquid air the substance changes from a deep orange to a light cream color. In order to see whether or not this change in color accompanies a transition from one form to another, and if so to determine the transition temperature, the following experiments were carried out.

Samples of the superoxide and of sodium chloride were put in a glass tube 7 mm in diameter, each in a layer 2 cm deep, with the two junctions of a differential thermocouple at the centers of the two layers, and the junction of another thermocouple (for measuring the temperature) at the center of one of the layers. The tube was sealed from the atmosphere by a plug of cotton followed by a layer of picin. The tube was enclosed in a copper jacket about 5 mm thick,

in order to insure a uniform heat transfer between the cell constants and the surroundings. Mercury was added as a further aid to this end and the whole was enclosed in a test tube. The thermocouples were single junction and were made of No. 32 copper and constantan wire joined with silver solder. The differential thermocouple was connected directly to a Leeds and Northrup Type R galvanometer which had a period of 5.5 sec. and a sensitivity of 2.7 mm/m per mv. The galvanometer scale was 60 cm from the instrument. No damping resistance was found necessary with this instrument. This differential thermocouple was used only as a means of observing differences of temperature between the oxide and the chloride. The actual temperature of the oxide was measured by means of the other thermocouple which was used in conjunction with a Leeds and Northrup Type K potentiometer. This thermocouple was calibrated by comparison with nine fixed points.

Warming curves were obtained from liquid air temperature to the temperature of melting ice. The cell was first cooled in liquid air for about an hour, the air was then removed from the enclosing Dewar flask, a cotton plug was inserted into the mouth of the flask to prevent irregular heating due to convection, and the cell was allowed to rise to room temperature. The most uniform curves were obtained when the time of warming over the temperature range studied was between 4 and 5 hours.

Cooling curves were obtained by enclosing the cell in an unsilvered Dewar flask and cooling by immersing this flask in liquid air. The flask that was used allowed the temperature of the cell to fall from room temperature to liquid air temperature in about 4 hours.

The warming curves and cooling curves all showed a pronounced break, corresponding to a transition at the temperature  $-75.5^\circ \pm 0.5^\circ \text{C}$ . (No break in this region was shown by control curves obtained by replacing the superoxide in the cell by sodium chloride.) Observation of the color change showed that it occurs at the same temperature, to within about  $\pm 15^\circ$ .

The experimental method is not sufficiently delicate to distinguish between a true polymorphic transition and a gradual transition;<sup>2</sup> if the transition is of the latter type, it is reasonably sharp, extending over a temperature range not greater than three or four degrees.

The normal superoxide ion is in the state  $^3\Pi$ , and the separation of the two levels  $^3\Pi_{1/2}$  and  $^3\Pi_{3/2}$  is probably about the same as for NO,  $121 \text{ cm}^{-1}$ . It is interesting to note that this energy value is equal to  $kT$  at the temperature  $T = 213^\circ \text{A}$ , only  $15^\circ$  from the observed transition temperature; though until more definite evidence is obtained the suggestion that the transition of the solid substance is related to the electronic transition of the molecules must be considered as speculative.

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March 15, 1935.

<sup>1</sup> E. W. Neuman, J. Chem. Phys. **2**, 31 (1934).

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