THE NORMAL VIBRATIONS OF MOLECULES HAVING OCTAHEDRAL SYMMETRY.

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1. Introduction.

About two years ago, Redlich, Kurz and Rosenfeld\(^1\) published their investigation of the Raman spectra of the ion SnCl\(_6\) contained in some molecules and of the molecule SbCl\(_5\). They also published the theoretical expressions for the frequencies of the AB\(_6\) model having octahedral symmetry under a simplified form of the central force system. Recently, Vost, Steffens and Gross\(^2\) have published their investigation over the Raman spectra of the hexafluorides of sulphur, selenium and tellurium along with their theoretical investigation of the normal modes of vibration of the regular octahedral model AB\(_6\) under the central force system. Their paper also contains the expressions for the frequencies of the normal modes under the valence force system as investigated by Bright Wilson, Jr. Very recently, Eucken and Ahrens\(^3\) have published with the collaborations of Bartholeme and Bewilogua an experimental paper over the Raman spectrum and the infra-red spectrum of sulphur hexafluoride. Regarding the structures of the molecules, the electron diffraction experiments by Brockway and Pauling\(^4\) and Braune and Knoke\(^5\) indicate that the hexafluorides of the sulphur group have octahedral symmetry. Watson, Rao and Ramaswamy\(^6\) find that the sulphur hexafluoride molecule has no permanent dipole moment which favours the octahedral symmetry of the molecule. That the molecules have the said symmetry has also been argued by Ruff\(^7\) and his collaborators from the point of view of molecular volumes.

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Theoretically, the regular octahedral \( \text{AB}_6 \) model has fifteen modes of vibration of which one is single and totally symmetrical, one is doubly degenerate and four others are triply degenerate. The single mode, the doubly degenerate mode and one of the triply degenerate modes are active in the Raman effect and inactive in the infra-red while two other types of the triply degenerate modes are inactive in the Raman effect and active in the infra-red. The one remaining triply degenerate mode is neither active in the Raman effect nor in the infra-red. Accordingly, the Raman spectra of the hexafluorides of sulphur, selenium and tellurium show three frequency shifts corresponding to the Raman active modes. The infra-red spectrum of sulphur hexafluoride shows main absorptions at 617 cm\(^{-1}\) and 965 cm\(^{-1}\) corresponding to the infra-red active modes. The theoretical expressions for the frequencies of the normal modes under the central force system are not in good agreement with the observed frequencies, for the calculated value of \( \nu_1 \) of sulphur hexafluoride is 1510 cm\(^{-1}\) while the observed value is 965 cm\(^{-1}\) according to Bucken and Ahrens. It has been found by many that the central force formulae are not in good agreement with the observed frequencies in the cases of some other molecules also. For example, the frequency of the totally symmetrical normal mode of the methane molecule is 4217 cm\(^{-1}\) according to the central force system while the observed strong frequency shift corresponding to the mode is at 2915 cm\(^{-1}\). Recently, the author has tried to explain the vibration spectra of the molecule methane and other allied molecules basing the constants of the potential energy function firstly on the three types of major forces, i.e., the primary valence forces, the directed valence forces and the repulsive forces, and secondly with a suitable type of intra-valence forces included with the major forces mentioned.

The purpose of this paper is to obtain the expressions for the frequencies of the normal modes of the \( \text{AB}_6 \) model having octahedral symmetry basing the constants of the potential energy function on the three types of major forces pointed out and some types of intra-valence forces. The various force constants of the sulphur hexafluoride molecule have been calculated. The probable positions of the frequencies of the infra-red active modes of the hexafluorides of selenium and tellurium are predicted.

In the case of a polyatomic molecule, one has to consider the three types of major forces comprised by the primary valence forces, the directed valence forces and the repulsive forces. Though the three forces' system is

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