

On the normal vibrations of nonrigid molecule $B(CH_3)_3$

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Abstract. Treating the symmetry operations as transformations in higher dimensional space, it is shown that Wigner's method can be straightaway extended to study the vibrations of nonrigid molecules exhibiting free or nearly free internal rotations. The molecule $B(CH_3)_3$ is illustrated.

Keywords. Isodynamic operation; symmetry group; symmetry coordinates; normal vibrations; non-rigid molecule.

1. Introduction

A complete analysis of the normal modes of oscillation of a molecule would be of great help in interpreting the Raman and infrared spectra. Wigner (1930) showed how group theory could be used effectively towards this end. Subsequently Tisza (1933), Wilson (1934), Placzek (1934), Rosenthal and Murphy (1936) made important contributions to the subject. Wilson (1934) applied Wigner's (1930) method to the benzene molecule and obtained its normal modes and frequencies. Rosenthal and Murphy (1936) made a detailed report on the subject—with the required elements of group theory and their representations—and showed the utility of the group theoretical method in solving the problem of molecular vibrations of polyatomic molecules. Later, the normal modes and frequencies of the sulphur molecule were worked out by Bhagavantam and Venkatarayudu (1938) using the same method. There has been much interest recently in the vibrations of nonrigid molecules which exhibit free or nearly free internal rotation (Hougen 1964; Bunker 1965; Fleming and Banwell 1969). Some of these studies suggest the possibility of extending Wigner's method to the case of nonrigid molecules also. In the present paper, the possibility of extending Wigner's group theoretical method to the problem of normal vibrations of the nonrigid molecule $B(CH_3)_3$ is studied and the selection rules for the Raman and infrared spectra of this molecule are worked out. The number of modes active in the infrared spectra agrees with the corresponding number experimentally reported by Stewart (1956).

2. Method of extension

Longuet-Higgins (1963) and Altmann (1967, 1971, 1977) obtained, in two different ways, the symmetry groups of nonrigid molecules with free or nearly free internal