GROUP THEORY FOR VARIOUS RAMAN SCATTERING PROCESSES

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1. INTRODUCTION

It is well known that the selection rules for the activity of vibrations of molecules in the Raman effect are different from those for infrared absorption. For molecules having a center of symmetry the principle of mutual exclusion holds: vibrations that are active in infrared absorption are inactive in the Raman effect and vice versa. Highly symmetric molecules may have quite a number of vibrations that are inactive in both effects, the so-called silent modes. Of the 20 vibrations of the benzene molecule, for instance, 4 are infrared active, 7 Raman active, and 9 silent modes.

The selection rules for the hyper Raman effect are governed by the transformation properties of the third rank tensor of the hyperpolarizability as opposed to the second rank tensor of the linear polarizability for the linear Raman effect and the vector of the dipole moment for infrared absorption. Therefore the selection rules are more relaxed and some of the "silent" modes become active in the hyper Raman effect and may be directly observed, as pointed out in the preceding and the following paper by D.A. Long.

Further silent modes may become observable through the second hyper Raman effect based on the fourth rank tensor of the second hyperpolarizability, therefore also the selection rules for this effect are considered here.

There exists an extended literature on group theoretical methods in molecular spectroscopy. Only the classical textbook

of Wilson, Decius, and Cross (1) and the corresponding chapters in the books on Raman spectroscopy by Brandmüller and Moser (2), Sushchinskij (3), and Long (4) shall be mentioned here. The selection rules for the hyper Raman effect were derived by Cyvin, Rauch, and Decius (5) and for the second hyper Raman effect by Christie and Lockwood (6). A quantum electrodynamical derivation of the hyper Raman selection rules, also for chiral molecules, can be found in papers by Andrews and Thirunamachandran (7).

Here a very simple explanation of group theoretical methods to calculate the number of vibrations of a molecule in the various irreducible representations (symmetry species) and their activity in infrared absorption, the linear Raman effect, and the first and second hyper Raman effect will be given without any mathematical proof. The Schoenflies notation common in molecular spectroscopy and the Hermann-Mauguin or international notation known from crystallography will be used in parallel.

Only vibrational selection rules and only symmetric tensors are considered here for simplicity. The rotational selection rules of the hyper Raman effect are treated in a review article by Altmann and Strey (8). Antisymmetric contributions to the polarizability occur in resonance Raman spectra (9). The antisymmetric components of the polarizability and first hyperpolarizability (6, 10) tensors are included in the tables of symmetry classes in Long's book (4). The selection rules for the first and second hyper Raman effect in crystals have been calculated by Winter (11) for the 32 crystallographic point groups using the method of the projection operator (12, 13). The resulting tables can be obtained by writing to Sektion Physik der Universität München, Lehrstuhl J. Brandmüller, Schellingstrasse 4/III, D-8000 München 40.

2. MOLECULAR SYMMETRY

Rigid molecules, and only these are considered here, can be transformed into identical configurations by symmetry operations. In every symmetry operation a point, a straight line (axis), a plane, or the whole space remain fixed; these geometrical elements are called symmetry elements. The symmetry operations are characterized by the symmetry elements of a molecule and form a group; because at least one point remains fixed in the operations, the group is called the point group of the molecule. In a molecular vibration the atoms are displaced from their equilibrium positions and the symmetry of the molecule is changed. According to their symmetry or antisymmetry with respect to the different symmetry elements the vibrations are grouped into the different symmetry species of a point group. The terminology will be explained using the examples