Calculation of Resonance Raman Cross Sections of ClO₂ Molecule

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Introduction

We calculate the absorption spectrum and cross sections of resonance Raman of ClO₂ molecule due to transition \( X^2B_1 < A^2A_2 \). We evaluate multi-dimensional time domain integrals that arise in the calculation of absorption cross section when the electronic transition takes place between displaced, distorted, rotated harmonic potential energy surfaces.

In this paper we focus on the model consisting of 3 vibrational modes.

We do ab initio calculations to determine the potential energy surfaces of two electronic states. The time-Correlation function formalism has been used to calculate resonance Raman cross sections and electronic absorption spectra of ClO₂ molecule.

The multi-dimensional time domain integrals that arise in these calculations have been evaluated for the cases in which electronic transitions take place between displaced, displaced-distorted, and displaced-distorted-rotated harmonic potential energy surfaces [1]. The evaluations include the effects of equilibrium displacements, normal-mode frequency shifts, as well as mixing of the normal coordinates upon the electronic excitations.

Results

Chlorine dioxide is a molecule with \( C_{2v} \) symmetry. It has 3 normal modes: Symmetric stretching with symmetry \( a_1 \), bending with symmetry \( a_1 \), and asymmetric stretching with symmetry \( b_2 \).

Excited electronic states will generally be rotated with respect to those of the ground state. Depending on the order of magnitude of the rotation, the Franck-Condon factors which determine the intensity distribution in electronic spectra, may change significantly and thereby cause a change in the vibrational structure of the spectra. The
explicit consideration of mode scrambling is thus a way to improve the absorption and cross sections of resonance Raman intensities. The absorption spectrum of ClO$_2$ in dilute solution shows a long vibrational progression up to 20 harmonics. The spectra calculated are in agreement with the experimental ones.

References