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The effective Hamiltonian for the coupling between inversion–torsion states of hydrazine

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Abstract

In the present paper, a procedure to calculate matrix elements of the group-theoretical Hamiltonian for hydrazine is described and explained in detail, and a complete set of rovibrational matrix elements responsible for interstate interactions is presented. The transformation properties of the framework functions under the symmetry operators of the double group $G_{16}^{(2)}$ are explained in a simple way using the MS Excel spreadsheet.

Keywords: Hydrazine; Effective Hamiltonian; Anharmonic and Coriolis resonances

1. Introduction

Hydrazine is a molecule for which the rovibrational spectrum is extremely complicated due to three large amplitude motions—two inversions of equivalent amino groups and torsion around the *N–N* axis. These three large amplitude motions are strongly coupled. The effective group-theoretical Hamiltonian proposed by Hougen [1] proved to be very successful in the interpretation of rotational and some rovibrational spectra of the ground and some excited torsional states of hydrazine, assuming that these states could be treated separately. The Hamiltonian did not work properly for the analysis of rovibrational spectra of excited inversion motions due to the couplings of these states with other vibrational states.

In the 730–1050 cm^{-1} region, three fundamental bands appear: the symmetric, ν_6, and antisymmetric, ν_{12}, wagging, and the third excited torsional state, $3\nu_7$ (Fig. 1). The band centers for these bands are located at 795, 937 and 860 cm^{-1}, respectively.

Whereas the antisymmetric wagging band is only slightly perturbed, the symmetric one shows a very strong Fermi perturbation. It was puzzling, because the energy separation between the wagging and the third excited torsional states were similar and the sublevels of all states posses all available symmetries of the $G_{16}^{(2)}$ symmetry group of hydrazine. The main reason, why the antisymmetric wagging band is almost unperturbed by the $3\nu_7$ state, contrary to the symmetric wagging, is a different symmetry of the ν_6 and ν_{12} states with respect to the C_2 axis of hydrazine. In this paper, it has been shown that there is a distinct difference in perturbation effects observed for both inversion states when coupled to the third torsional state.

The aim of this work was to develop the matrix Hamiltonian elements for two resonating states and two general cases were considered. In the first one, the matrix elements for the symmetric inversion state ν_6 and the third torsional state $3\nu_7$ were calculated, where both states are symmetric with respect to the rotation about the C_2 axis of hydrazine. This type of interaction is called an A–A resonance. In the second case, the resonance between the state ν_{12}, antisymmetric with respect to the rotation about the C_2 axis, and $3\nu_7$ was taken into account—this is a B–A type resonance. The structure of the matrix elements for

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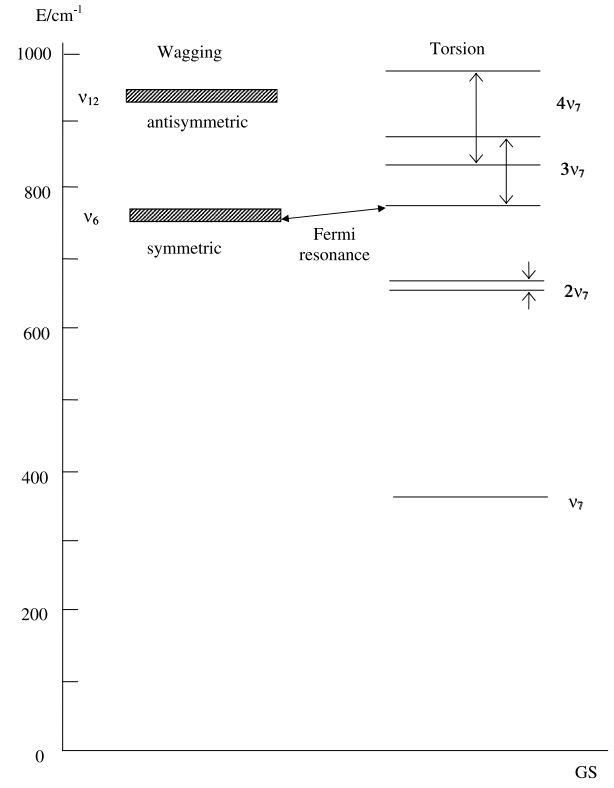

Fig. 1. Energies of the wagging–torsional states of hydrazine.

interactions between states of the same symmetry, i.e. for the coupling of A–A or B–B type, is similar to the elements derived earlier by Ohashi and Masue [2] for a single vibrational state. Those have been recalculated and some small differences between the new set of matrix elements and those calculated in [2] have been noticed. The matrix elements for the coupling between A and B symmetry states have completely different structure and have been derived in this paper for the first time.

Although the derivation of the matrix elements was systematically presented in previous papers [1,2] for the G_{16} group of hydrazine, it has not been so obvious for the $G_{16}^{(2)}$ group. In this paper a new technique leading to a derivation of necessary matrix elements is shown. It seems that the extensive use of the Excel spreadsheet program makes the systematic calculation of matrix elements relatively simple.

2. Qualitative discussion of the results of this paper

As far as the results are concerned, we list here three topics that were found to be surprising.

The first thing that struck us, was the fact that the forms of the interaction terms in $G_{16}^{(2)}$ are quite different for couplings between vibrational states which were originally A–A or A–B type in C_2. If hydrazine were a rigid molecule, it would be described by the C_2 point group. Whereas A–A or B–B type interactions in C_2 can be either purely vibrational, with shifts being some fraction of the vibrational spacings (and therefore large), or rovibrational (Coriolis), with shifts being some fraction of the rotational spacings (and therefore small), the A–B or B–A interactions in C_2 cannot be purely vibrational, only rovibrational. Since hydrazine tunnels, it belongs to the permutation–inversion group $G_{16}^{(2)}$, so the coupling terms in $G_{16}^{(2)}$ differ between A–A or B–B type interactions and A–B or B–A because of the influence of the rigid-molecule C_2 selection rules on this floppy-molecule permutation–inversion group.

Another surprise concerns the behavior of matrix elements for even K and odd K states. They are quite different. This may be somehow connected with the fact that a X_2Y_4 molecule with D_{4h} equilibrium structure (Y_4 square with one X above and below the plane) or a molecule described by the D_{2d} point group (allene) would also belong to G_{16}, and then $K =$ even rotational functions of this symmetric top would then be non-degenerate (A and B species) while $K =$ odd functions would be doubly degenerate (E species) [3].

It will be shown that the $G_{16}^{(2)}$ group is not sufficient for the derivation of matrix elements. The use of time reversal eliminates a surprisingly large number of matrix elements permitted by the $G_{16}^{(2)}$ group. Again, for rigid molecules, except for a few rare molecular symmetries like the "pinwheel groups" C_n, point group considerations are usually sufficient to obtain all Hamiltonian matrix elements selection rules. These LAM problems seem to be different for some reason.

3. Phenomenological effective operator

To explain the interactions between wagging–torsion–rotation states we follow the idea of the group-theoretical phenomenological Hamiltonian developed originally by Hougen [1], which can be presented in the following form:

$$\begin{aligned}\hat{W} = \sum_{n=1}^{8} & wh_{nv} + wh_{nj}J^2 + wh_{nk}J_z^2 + wh_{njj}J^4 + wh_{njk}J^2J_z^2 \\ & + wh_{nkk}J_z^4 + wf_n(J_+^2 + J_-^2) + wg_n[\mathrm{i}(J_+^2 - J_-^2)] \\ & + wq_nJ_z + wd_n(J_+^4 + J_-^4) + wp_n[\mathrm{i}(J_+^4 - J_-^4)] \\ & + [wr_{n+}J_+ + wr_{n-}J_-] + [ws_{n+}(J_zJ_+ + J_+J_z) \\ & + ws_{n-}(J_zJ_- + J_-J_z)] \end{aligned} \quad (1)$$

where the subscript n indicates different groups of interaction parameters. The ($n = 1$) parameters involve no tunneling and can be considered as usual Fermi or Coriolis type coupling parameters. The ($n = 2$) parameters describe coupling involving also inversion motion of both NH_2 groups, ($n = 3$) involving internal rotation tunneling through the trans barrier, ($n = 4$) internal rotation and inversion of both NH_2 groups, ($n = 5, 6$) inversion of one NH_2 group, and ($n = 7, 8$) internal rotation and inversion of one NH_2 group. Eq. (1) is formally identical to Eq. (18) in Ref. [1] but the meaning of parameters is different, since they describe couplings between vibrational states