EFFECTIVE HAMILTONIANS FOR STATES INTERACTING BY MEANS OF FERMI RESONANCE

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INTRODUCTION

This poster represents a compact study of anharmonic resonances among A_1 and E vibrations in C_{3v} molecules. We studied the following cases of anharmonic resonance: (i) the fundamental band interacting with an overtone, (ii) the fundamental band interacting with a combination band.

The fundamental band: totally symmetric $v_n(A_1)=1$ or degenerate $v_t(E)=1$.

The overtone: $v_n(A_1)=2$ or $v_t(E)=2$.

The combination band: $v_n(A_1)=1, v_{n'}(A_1)=1$ or $v_n(A_1)=1, v_t(E)=1$ or $v_t(E)=1, v_{t'}(E)=1$.

TREATED CASES

1. $\nu_n(A_1)\leftrightarrow\nu_{n'}(A_1)+\nu_{n''}(A_1)$
2. $\nu_n(A_1)\leftrightarrow 2\nu_{n'}(A_1)$
3. $\nu_n(A_1)\leftrightarrow\nu_{n'}(A_1)+\nu_t(E)$
4. $\nu_n(A_1)\leftrightarrow\nu_t(E)+\nu_{t'}(E)$
5. $\nu_n(A_1)\leftrightarrow 2\nu_t(E)$
6. $\nu_t(E)\leftrightarrow\nu_n(A_1)+\nu_{t'}(E)$
7. $\nu_t(E)\leftrightarrow\nu_n(A_1)+\nu_{n'}(A_1)$
8. $\nu_t(E)\leftrightarrow 2\nu_n(A_1)$
9. $\nu_t(E)\leftrightarrow\nu_{t'}(E)+\nu_{t''}(E)$
10. $\nu_t(E)\leftrightarrow 2\nu_{t'}(E)$

FERMI RESONANCE

Fermi resonance is a third-rank resonance, which occurs in the case of accidental near-degeneracies of the type $\omega_k \simeq \omega_l + \omega_m$.
Fermi resonance is a source of information on the potential energy function, it gives very direct information on specific cubic potential constants.

$$k_{klm} = \left(\frac{\partial^3 V}{\partial q_k \partial q_l \partial q_m}\right)_e \approx \kappa\omega_{vib}$$
$$f_{31} \approx \kappa^3\omega_{vib}$$
$$k^J_{klm}, k^K_{klm}, f_{32} \approx \kappa^5\omega_{vib}$$

THEORY

The Hamiltonian for the resonance problem can be split into the components: $\mathbf{H}=\mathbf{H}_1+\mathbf{H}_2+\mathbf{H}_{int}$ (Eq.(1))
where $\mathbf{H}_1$ is the rovibrational Hamiltonian for the first state (A_1 or E fundamental), $\mathbf{H}_2$ is the rovibrational Hamiltonian for the second state (overtone or combination), and $\mathbf{H}_{int}$ is the rovibrational Hamiltonian for the interaction between the two vibrational states.

We have considered the three lowest terms ($\mathbf{H}_{int}=\mathbf{H}_{30}+\mathbf{H}_{31}+\mathbf{H}_{32}$) in the interaction Hamiltonian ($\mathbf{H}_{vr}$ in thetandard Watson notation). It follows from the symmetry considerations that not all these terms have to be necessarily present in all cases. The $\mathbf{H}_{31}$ terms are usually denoted as the higher-order Coriolis terms (like all terms, which are linear in rotational angular momentum).

In addition, we have to consider also the limitations due to the possible indeterminacies caused by existence of the block-diagonal transformation operators. Watson has shown[1,2] that indeterminacies among the molecular parameters follow from the existence of a unitary transformation of the effective Hamiltonian **H**:

$$\tilde{\mathrm{H}} = \exp(i\mathrm{S})\mathrm{H}\exp(-i\mathrm{S}) == \mathrm{H} + [i\mathrm{S},\mathrm{H}] + \frac{1}{2}[i\mathrm{S},[i\mathrm{S},\mathrm{H}]] + \ldots \quad \text{(Eq.(2))}$$

The block diagonal operator **S**, which must be Hermitian, invariant to the all operations of the molecular symmetry group and change sign under the time-reversal operation has similar structure to the Hamiltonian.

APPLICATIONS

Rovibrational spectroscopy of the Fermi-interacting v_4 = 1 and v_3 = v_6 = 1 levels of DCF_3 (Petr Pracna, Adina Ceauscu-Velcescu, Adriana Predoi-Cross). This is the symmetry case numbered 6. in this poster. Recent development of this study is presented in poster K 20.
The states lie very close and therefore the interaction is strong. It was necessary to add interaction terms up to higher order ($\mathbf{H}_{30}$, $\mathbf{H}_{31}$, $\mathbf{H}_{32}$, $\mathbf{H}_{33}$). Two reduction schemes were designed and the testing of the relations between them will follow.

CONCLUSIONS

The MAPLE program has been applied to evaluate the commutators in Eq.(2). Clearly, the transformation operators cubic in vibrational operators cannot affect the molecular parameters in the quasi-diagonal blocks, and for these parameters the *Q-Reduction*, the *D-Reduction* or the *L-Reduction* should be employed independently.
The parameters of the $\mathbf{S}_{30}$ and $\mathbf{S}_{31}$ operators have to be determined by the constraints in the interaction blocks.
The reduction schemes for the individual studied resonance cases are specified bellow.

	Reduction scheme I	Reduction scheme II	***S*** parameters to be determined
$\nu_n(A_1)\leftrightarrow\nu_{n'}(A_1)+\nu_{n''}(A_1)$	$k_{nn'n''}$, $k^J_{nn'n''}$	$k_{nn'n''}$, $k^K_{nn'n''}$	s_{30}
$\nu_n(A_1)\leftrightarrow 2\nu_{n'}(A_1)$	$k_{n2n'}$, $k^J_{n2n'}$	$k_{n2n'}$, $k^K_{n2n'}$	s_{30}
$\nu_n(A_1)\leftrightarrow\nu_{n'}(A_1)+\nu_t(E)$	f^x_{31}	---	s_{31}
$\nu_n(A_1)\leftrightarrow\nu_t(E)+\nu_{t'}(E)$	$k_{ntat'a}$, $k^J_{ntat'a}$, f^x_{31}, f^{xy}_{32} fails if $(A\zeta - A\zeta')$ is 'small'	$k_{ntat'a}$, $k^J_{ntat'a}$, $k^K_{ntat'a}$, f^z_{31}, f^x_{31} (last constraint from $\mathbf{H}_{33}$)*	s_{30}, (s^z_{31})*, s^x_{31}
$\nu_n(A_1)\leftrightarrow 2\nu_t(E)$	k_{n2ta}, k^J_{n2ta}, k^K_{n2ta}, f^x_{31}	k_{n2ta}, k^J_{n2ta}, f^x_{31}, f^{xy}_{32} or k_{n2ta}, k^K_{n2ta}, f^x_{31}, f^{xy}_{32}	s_{30}, s^x_{31}
$\nu_t(E)\leftrightarrow\nu_n(A_1)+\nu_{t'}(E)$	$k_{ntat'a}$, $k^J_{ntat'a}$, f^x_{31}, f^{xy}_{32} fails if $(A\zeta - A\zeta')$ is 'small'	$k_{ntat'a}$, $k^J_{ntat'a}$, $k^K_{ntat'a}$, f^z_{31}, f^x_{31} (last constraint from $\mathbf{H}_{33}$)*	s_{30}, (s^z_{31})*, s^x_{31}
$\nu_t(E)\leftrightarrow\nu_n(A_1)+\nu_{n'}(A_1)$	f^x_{31}	---	s_{31}
$\nu_t(E)\leftrightarrow 2\nu_n(A_1)$	f^x_{31}	---	s_{31}
$\nu_t(E)\leftrightarrow\nu_{t'}(E)+\nu_{t''}(E)$	$k_{tat'at''a}$, $k^J_{tat'at''a}$, f^{xa}_{31}, f^{xb}_{31}, f^{xc}_{31}, f^{xxa}_{32}, f^{xxb}_{32}, f^{xxc}_{32}	$k_{tat'at''a}$, f^z_{31}, f^{xa}_{31}, f^{xb}_{31}, f^{xc}_{31}, f^{xxa}_{32}, f^{xxb}_{32}, f^{xxc}_{32}	s_{30}, s^z_{31}, s^{xa}_{31}, s^{xb}_{31}, s^{xc}_{31}
$\nu_t(E)\leftrightarrow 2\nu_{t'}(E)$	$k_{ta2t'a}$, $k^J_{ta2t'a}$, f^{xa}_{31}, f^{xb}_{31}, f^{xxa}_{32}, f^{xxb}_{32}	$k_{ta2t'a}$, f^z_{31}, f^{xa}_{31}, f^{xb}_{31}, f^{xxa}_{32}, f^{xxb}_{32}	s_{30}, s^z_{31}, s^{xa}_{31}, s^{xb}_{31}

RELATED WORKS

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