A Global Algebraic Treatment for \(XY_2\) Molecules: Application to \(D_2S\).

O.V. Gromova\textsuperscript{a,b}, F. Michelot\textsuperscript{a}, C. Leroy\textsuperscript{a,*}, O.N. Ulenikov\textsuperscript{b}, Y. Pashayan-Leroy\textsuperscript{a}, E.S. Bekhtereva\textsuperscript{b}

\textsuperscript{a} Institut Carnot de Bourgogne, UMR 5209 CNRS-Université de Bourgogne, BP 47870, 21078 Dijon Cedex, France
\textsuperscript{b} Laboratory of Molecular Spectroscopy, Physics Department, Tomsk State University, 634050 Tomsk, Russia.

Abstract

We suggest to use for \(XY_2\) molecules some results previously established in a series of articles for vibrational modes and electronic states with an \(E\) symmetry type. We first summarize the formalism for the standard \(u(2) \supset su(2) \supset so(2)\) chain which, for its most part, can be kept for the study of both stretching and bending modes of \(XY_2\) molecules. Next the also standard chain \(u(3) \supset u(2) \supset su(2) \supset so(2)\) which is necessary, within the considered approach, is introduced for the stretching modes. All operators acting within the irreducible representation (irrep) \([N00] \equiv [N\dot{0}]\) of \(u(3)\) are built and their matrix elements computed within the standard basis. All stretch-bend interaction operators taking into account the polyad structure associated with a resonance \(\omega_1 \approx \omega_3 \approx 2\omega_2\) are obtained. As an illustration, an application to the \(D_2S\) molecular system is considered, especially the symmetrization in \(C_2v\). It is shown that our unitary formalism allows to reproduce in an extremely satisfactory way all the experimental data up to the dissociation limit.

Key words: Vibrational excitations; Unitary group approach; Local mode; Normal mode; \(D_2S\); Dissociation limit

\textit{PACS:} 33.20.Tp; 03.65.Fd

1. Introduction

The hydrogen sulfide molecule and its isotopic species are of interest for terrestrial atmospheric pollutant measurements. As this gas is more heavy than air, it remains concentrated to the floor level and can be lethal at high concentration. Global warming process has increased the number of studies devoted to the chemical and physical properties of \(H_2S\) and isotopic species \([1, 2, 3]\). These molecules have also been observed in planet atmospheres like Jupiter \([4]\) or Venus \([3]\) and appear in the analysis of the interstellar medium \([6, 7, 8]\).

Many papers, devoted to the analysis of the rovibrational spectra of \(D_2S\), have been published during the last thirty years: anharmonicity corrections to observed fundamental frequencies of vibration in \([3]\), various molecular structures have been evaluated in \([10, 11]\) for the \(\nu_2\) band, \([12]\) for the three fundamental bands \(\nu_2, \nu_1\) and \(\nu_3\) of \(D_2^{32}S\) and the \(\nu_2\) band of \(D_2^{34}S\), application of the MORBID (Morse Oscillator Rigid Render Internal Dynamics) computer program for the four isotopic molecules \(H_2^{32}S, D_2^{32}S, HD^{32}S,\) and \(H_2^{34}S\) \([13]\).

Different theoretical models have been elaborated to improve the analysis of \(D_2S\) \([14]\) or bent \(XY_2\) molecules in general \([15, 16]\). Initiated by the early works of Iachello and Oss \([16]\), algebraic formalisms seem to be good tools for the description of \(XY_2\) molecules \([17]\) particularly to take into account the local behavior. Also the vibrational spectrum must be described using a Hamiltonian where the importance of Fermi-type interaction is taken into account \([18]\). Other studies using potential energy surface have been recently published \([19, 20]\). This last method is particularly adapted when one has many data coming from different isotopic species. For further references about re-
cent analysis of $H_2S$ molecule and isotopes, the reader is
invited to examine the references given in  \[11\] \[13\] \[20\].
In this paper, we use and adapt formalisms that we de-
veloped previously. Some of them dealt with unitary algebras
applied in molecular spectroscopy \[21\] \[22\], pure algebraic
studies \[23\] or works concerning algebraic chains which
may be adapted to $XY_2$ systems \[24\] \[25\] \[26\].
In the theoretical part we use the properties of two alge-
braic chains, $u(2) \supset su(2) \supset so(2)$ and $u(3) \supset u(2) \supset
su(2) \supset so(2)$, to analyze the bending and stretching vi-
brational modes of bent $XY_2$ systems. Basis states and
operators oriented in these chains are built and the matrix
elements of the oriented operators are given. Next sym-
metrization of these tensors in $C_2v$, allows to build Hamil-
tonian and tensor operators adapted to the $C_2v$, molecular
point group. A method to select, in the $u(3) \otimes u(2)$ dy-
amical algebra, all relevant operators for a given polyad
structure is proposed and applied to the case of a 2:1 res-
sonance.
As an illustration, in the last section our approach is tested
upon the $D_2S$ molecule. The experimental data are repro-
duced with a standard deviation close to 0.5 cm$^{-1}$ and the
calculated dissociation energy is found close to the ex-
perimental one.

2. Theoretical frame

2.1. The standard $u(2) \supset su(2) \supset so(2)$ chain
We consider first physical systems under the assump-
tion that they can be described from two boson creation
and annihilation operators denoted $b_i^+$ and $b_i$ ($i = 1, 2$)
which satisfy the usual Bose commutation relations.
A basis for the space of states may be obtained through re-
peated action of $b_1^+$ and $b_2^+$ onto the vacuum state $|0, 0\rangle$:

$$|n_1, n_2\rangle = (n_1! n_2!)^{-1/2} b_1^{n_1} b_2^{n_2} |0, 0\rangle .$$  \[1\]

We note that these states may be taken as those of a two di-
mensional oscillator (within a usual approach) or as those
of two one dimensional oscillators. They will also be as-
associated with the dynamical states for a one dimension-
 oscillator.

Tensor operators are built from the well-known Schwinger’s
realization of $su(2)$ in terms of two boson operators \[27\]:

$$J_+ = b_1^+ b_2 , \quad J_- = b_1^+ b_1$$
$$J_z = \frac{1}{2} (N_1 - N_2) = \frac{1}{2} (b_1^+ b_1 - b_2^+ b_2) ,$$  \[2\]

with commutation relations

$$[J_z, J_\pm] = \pm J_\pm , \quad [J_+, J_-] = 2 J_z,$$

and $u(2)$ is obtained with the addition of the linear invari-
ant $N = N_1 + N_2$, with $N_i |n_1, n_2\rangle = n_i |n_1, n_2\rangle$ ($i = 1, 2$).

2.1.1. General tensor operators and states within the stan-
dard chain
Keeping with previous conventions \[24\] covariant $su(2)$
states $|jm\rangle$ and operators $T^{(j)}_m$ are characterized by the
relations ($m : -j, \cdots , j$):

$$J_\pm |jm\rangle = -m |jm\rangle,$$
$$J_\pm |jm\rangle = -[(j \pm m)(j \mp m + 1)]^{1/2} |jm \mp 1\rangle,$$

and likewise for irreducible tensor operators (ITO)

$$[J_z, T^{(j)}_m] = -m T^{(j)}_m,$$
$$[J_\pm , T^{(j)}_m] = -[(j \pm m)(j \mp m + 1)]^{1/2} T^{(j)}_{m \mp 1}.$$  \[4\]

In the whole $u(2) \supset su(2) \supset so(2)$ chain, symmetrized
states and tensor operators are further characterized by an
additional $u(2)$ label $[m_{12} m_{22}] = [m_1 - m_2]$ in Gel’fand
notation \[28\] \[29\] with $j = (m_1 + m_2)/2$ and

$$[N_i, [m_1 - m_2] T^{(j)}_{-j}] = m_{i2} [m_1 - m_2] T^{(j)}_{-j} \quad i = 1, 2.$$  \[5\]

With equations \[3\] \[4\] it can be checked that a realization
for the extremal components appearing in \[5\] is given by:

$$T \begin{pmatrix} m_1 - m_2 \\ m_1 \end{pmatrix} = (-1)^{m_2} m_1 ! m_2 ! [-\frac{1}{2} b_1^{m_1} b_2^{m_2} (m_1 - m_2)].$$  \[6\]

This allows to generate two sets of fundamental operators

$$[m_1, 0] T^{(j)}_m = (-1)^{m_1 + m} [(m_1^2 - m)(m_1^2 + m)!]^{-1/2} \times b_1^{(m_1 + m)} b_2^{(m_1 - m)} ,$$  \[7\]

2
\[ [0 - m_2] T^{(j)}_m = \left(-1\right)^{m_2} \left[ \frac{m_2 - m}{2} \right] \left( \frac{m_2 + m}{2} \right)! \left( \frac{m_2}{2} \right)^{1/2} \times b_1 \left( \frac{m_2 + m}{2} \right) b_2 \left( \frac{m_2 - m}{2} \right), \]

with \( j = m_2/2 \). In particular the standard covariant basis is obtained with (17) acting upon the vacuum state:

\[ \langle n^0|T_m^{(j)}|0, 0 \rangle = (-1)^{2j+m}|j-m, j+m\rangle. \]

From the previous set (15,16) one may build all functionally independent operators which may act within the \( [n^0] \) of \( u(2) \) through

\[ [m_1 - m_2] T_m^{(j)} = i^{j-j_{\text{max}}} \left[ m_1^0 T^{(j)} \times [0 - m_2] T^{(j)} \right]_m^{(j)} \]

with

\[ j_{\text{min}} = \frac{m_1 - m_2}{2} \leq j \leq \frac{m_1 + m_2}{2} = j_{\text{max}}. \]

Their expansion in normal ordered form can easily be obtained; alternatively they may be written

\[ [m_1 - m_2] T_m^{(j)} = \left( m_1 m_2 \right) g_{ij} \left( N_1 + N_2 \right) \left[ m_1^i - m_2^j \right] T_m^{(j)}, \]

where

\[ m_1^i = \frac{m_1 - m_2}{2} + j, \quad m_2^j = \frac{m_2 - m_1}{2} + j, \]

hence \( j = (m_1^i + m_2^j)/2 \). \( \{ m_1 m_2 \} g_{ij} \) is a polynomial function of the \( u(2) \) linear invariant \( N_1 + N_2 \) given by:

\[ \left( m_1 m_2 \right) g_{ij} \left( N_1 + N_2 \right) = \left( \frac{(2j + 1)!}{(j_{\text{max}} + j + 1)! \left( j_{\text{max}} - j \right)!} \right)^{1/2} \times (N_1 + N_2)^{j_{\text{max}} - j}, \]

where \( X^{[k]} = X \times (X - 1) \times ... \times (X - k + 1) \).

We note that when \( j = j_{\text{max}} \), the operator (13) reduces to the identity and

\[ [m_1 - m_2] T_m^{(j_{\text{max}})} = [m_1 - m_2] T_m^{(j_{\text{max}})}, \]

the minimal covariant component of which is given by (15).

All phase conventions have been settled so that under hermitian conjugation (\( \dagger \)) and time reversal (\( \mathcal{K}_t \)) we have

\[ [m_1 - m_2] T_m^{(j)} = (-1)^{j-m} \left[ [m_1 - m_2] T_m^{(j)} \right]^\dagger, \]

\[ \mathcal{K}_t [m_1 - m_2] T_m^{(j)} \mathcal{K}_t^{-1} = (-1)^{m_1} [m_1 - m_2] T_m^{(j)}. \]

### 2.1.2. Matrix elements within the standard basis

With the Wigner-Eckart’s theorem we have in terms of \( su(2) \) Clebsch-Gordan coefficients (CG) (17):

\[ \langle [n^0] m'' | T^{(j)}_m | [n^0] j' m' \rangle = \left( 2 j'' + 1 \right)^{-1/2} \times C_{m m'}^{m''} (j'')^* \left( [n^0] m'' | T^{(j)}_m | [n^0] j' \right) \]

\[ = F_{m m'}^{m''} \left( [n^0] j' m' \right)^* \left( [n^0] j' m' \right) \times (2j'' + 1)^{-1/2} \left( [n^0] j' m' \right) \left( [n^0] j' m' \right), \]

where \( \ast \) denotes complex conjugation. The notation for the \( F \) symbols, which retains the full \( u(2) \supset su(2) \) labels, is useful when symmetry adaptation in a point group is performed. Reduced matrix elements (RME) for all operators are obtained with

\[ \left( [n^0] j' m' \right)^* \left( [n^0] j' m' \right) = \delta_{n', n'' + m_1 - m_2} \times \left( 2j'' + 1 \right)^{-1/2} \left( [2j + 1] (n' + m_1')! (n' - m_1')! \right)^{1/2}. \]

### 2.2. Tensors adapted to an \( u(3) \) dynamical algebra

For the applications we have in mind, the initial assumptions are the following:

- A molecule, with point group symmetry \( G \) (\( G = C_{2v} \)), admits in its full vibrational representation two non degenerate modes with close enough frequencies.

- The interaction of these modes with other vibrational modes is sufficiently low so that in first approximation it can be neglected. As a consequence a separate study taking into account the degrees of freedom associated with these modes only is possible.

- This study, made within the frame of an \( u(p+1) \) dynamical approach, requires the introduction of a dynamical or non-invariance \( u(3) \) algebra to which we associate the elementary boson operators \( \{ b_i^+, b_i \}_{i=1,2,3} \).

#### 2.2.1. The algebraic chain \( u(3) \supset u(2) \supset su(2) \supset so(2) \)

From the preceding assumptions the space of states is a carrier space for the so-called totally symmetric (or most
| canonical chain. The notation $|N\hat{0}\rangle$ of $u(3)$ which subduces to $|n\hat{0}\rangle$ ($n = 0, 1, \cdots N$) in $u(2)$ [29, 31]. Then all operators which may act within this $irrep$ are of symmetry $[z, 0, -z]$ with $z = 0, 1, \ldots, N$ (see [24, 32, 33] for more details).

Those which are maximal in $u(3)$ have the form:

$$
T \left[ \begin{array}{c}
[z \ 0 \ -z] \\
(m_1 - m_2)
\end{array} \right] = \left( \begin{array}{c}
\frac{m_1 + m_2 + 1}{N(N-z)!} \\
N!
\end{array} \right)^{1/2} b_1^z b_2^z,
$$

(19)

where the $\alpha_z, N$ coefficient is determined through the following normalization condition:

$$
< n, 0, N-n | T \left[ \begin{array}{c}
[z \ 0 \ -z] \\
(m_1 - m_2)
\end{array} \right] | 0, 0, N > = \delta_{z,n}.
$$

(20)

The notation $|n_1, n_2, n_3\rangle$ for the states is that of the $u(3)$ canonical chain. $|0, 0, N\rangle$ and $|n, 0, N-n\rangle$ represent respectively the state with zero excitation quantum and the state with $n$ excitation quanta maximal in $u(2)$. Then the semi-maximal operators of the $u(3)$ dynamical algebra write as:

$$
T \left[ \begin{array}{c}
[z \ 0 \ -z] \\
(m_1 - m_2)
\end{array} \right] = G(z, m_1, m_2) b_1^{m_1} b_2^{m_2},
$$

(21)

where $G(z, m_1, m_2)$ is an operator valued function invariant in $u(2)$ and defined by:

$$
G(z, m_1, m_2) = \left[ \begin{array}{c}
\frac{m_1 + m_2 + 1}{N(N-z)!} \\
N!
\end{array} \right]^{1/2} \times \left\{ \sum_{t=0}^{u} \frac{(-1)^{t+m_2}}{(m_1 + m_2 + 1)!} \times \begin{array}{c}
\frac{(z-m_1)!}{(z-m_2)!} \\
(N_1 + N_2 - m_1)!
\end{array} \times \begin{array}{c}
\frac{(z-m_2)!}{(z-m_2-t)!} \\
\times (N_3 - z + m_1 + u)\!
\end{array}
\right\} b_3^{-z-m_1-u} b_1^{-z-m_2-u}.
$$

(22)

with $u = \inf(z - m_1, z - m_2)$. From equations (6, 14) it appears the left member of equation (21) is, within a phase factor, the minimal covariant component of an ITO within the $su(2) \supset so(2)$ chain. So from the results in section 2.1.1 and taking into account that $G(z, m_1, m_2)$ commutes with the $su(2)$ ladder operators $J_+$ and $J_-$, an

arbitrary covariant operator is obtained through:

$$
T \left[ \begin{array}{c}
[z \ 0 \ -z] \\
[m_1 - m_2]
\end{array} \right] (j) = (-1)^{m_2} m_1! m_2!^{1/2} \times G(z, m_1, m_2) [m_1 - m_2] T_m^{(j)},
$$

(23)

where the various labels may take the values $0 \leq z \leq N$, $0 \leq m_1 \leq z$, $0 \leq m_2 \leq z$, $j = (m_1 + m_2)/2$, $-j \leq m \leq j$.

The phase of the preceding operators have been chosen so that

$$
T \left[ \begin{array}{c}
[z \ 0 \ -z] \\
[m_1 - m_2]
\end{array} \right] (j) = (-1)^{j+m} i^{m_1 - m_2} \times T \left[ \begin{array}{c}
[z \ 0 \ -z] \\
[m_2 - m_1]
\end{array} \right] (j),
$$

(24)

$$
\mathcal{K}_t T \left[ \begin{array}{c}
[z \ 0 \ -z] \\
[m_1 - m_2]
\end{array} \right] (j) \mathcal{K}_t^{-1} = (-1)^{m_1} \times T \left[ \begin{array}{c}
[z \ 0 \ -z] \\
[m_1 - m_2]
\end{array} \right] (j).
$$

(25)

2.2.2. Matrix elements

The covariant states, associated with the representation $[N\hat{0}]$ of $u(3)$ and adapted to the subduction $u(3) \supset u(2) \supset su(2) \supset so(2)$, are denoted $|[N\hat{0}][n0][jm]\rangle$ in the following. They may be generated from the zero quantum excitation state $|[N\hat{0}][00][00]\rangle \equiv |0, 0, N\rangle$, through the relation:

$$
|[N\hat{0}][n0][jm]\rangle = T \left[ \begin{array}{c}
n0 - n \\
[n0]
\end{array} \right] |[N\hat{0}][00][00]\rangle.
$$

(26)
The matrix elements for operators (23), computed in basis (20), are then given by:

\[ \langle [N \hat{0} \mid n'' \rangle j'' m'' | T \left[ \begin{array}{c} z \\ m \end{array} \right] \rangle = (2j'' + 1)^{-1/2} \hat{C}^{m \rightarrow m'}_{j' j''} \times \langle [N \hat{0} \mid n' \rangle j' m' | T \left[ \begin{array}{c} z \\ m \end{array} \right] \rangle \]

\[ \times \left[ (2j' + 1)^{-1/2} \hat{C}^{m \rightarrow m'}_{j' j''} \times \langle [N \hat{0} \mid n' \rangle j' m' | T \left[ \begin{array}{c} z \\ m \end{array} \right] \rangle \right] \]

where the remaining \( rme \) is given by (18), with \( m'_1 = m_1, m'_2 = m_2 \).

3. Application to \( XY_2 \) molecules

We make the assumption that an appropriate dynamical algebra for the description of the vibrational spectrum of these molecules is \( u(3)_S \times u(2)_B \), where the indices \( S \) and \( B \) respectively refer to stretching and bending modes. Below, we first specify the notations which are used in for each type of mode and next perform the symmetry adaptation in \( C_{2v} \) for states and operators.

3.1. Bending mode \( \nu_2 \)

3.1.1. Standard states and operators

For the Schwinger’s realization of \( su(2)_B \) we take (2):

\( (b) j_+ = b_+ b_5 \), \( (b) j_- = b_5^* b_4 \)

\( (b) j_z = \frac{1}{2}(N_4 - N_5) = \frac{1}{2}(b_4^* b_5 - b_5^* b_4) \),

and \( (b) j_z^2 = N_4 + N_5 = \hat{N}_b \) for the \( u(2)_B \) linear invariant. The standard covariant basis (30) is written \( (N_b = 2J_b) \):

\[ \langle [N_b \hat{0} \mid j_b m_b) = (-1)^{2J_b + m} | j_b - m, J_b + m > \]

\[ = \frac{(-1)^{2J_b + m}}{(J_b + m)! (J_b - m)!} \hat{C}^{m \rightarrow m'}_{j' j''} \times b_4^{+ j_b - m} b_5^{+ j_b + m} | 0, 0 > \] (29)

We may also set

\[ J_b - m = n_4 = \nu_2 \]

\[ J_b = \frac{n_4 + n_5}{2} = \frac{N_b}{2} \]

\[ \Leftrightarrow \]

\[ J_b + m = n_5 = N_b - \nu_2 \]

\[ m = \frac{n_5 - n_4}{2} = \frac{N_b}{2} - \nu_2 \]

Thus all results of section (21) can be used with the appropriate change of indices. However as \( N_b \) is associated with the maximal number of bending states and that only operators acting within the \( [N_b \hat{0} \) irrep of \( u(2) \) are allowed we necessarily have \( m_4 = m_5 \) for the general operators built before. The vibrational operators are thus \( (0 \leq j_b \leq m_4) \)

\[ [m_4 - m_4] B(j_m) = \hat{g}_{j_m} (N_4 + N_5) \]

\[ \times \left( m_4 - m_4 \right) B(j_m) \]

with \( m'_1 = m_1, m'_2 = m_2 \).

Their expanded expression in normal ordered form is:

\[ [m_4 - m_4] B(j_m) = \sum_{q_1, q_2} i^{2q_1} \left( \frac{m_4}{2} - q_1 \right)! \left( \frac{m_4}{2} + q_1 \right)! \times \left( \frac{m_4}{2} - q_2 \right)! \left( \frac{m_4}{2} + q_2 \right)! \]

\[ \times \left( \frac{m_4}{2} - q_1 \right)! \left( \frac{m_4}{2} + q_2 \right)! \]

\[ \times b_4^{+ j_b - m} b_5^{+ j_b + m} b_4^{+ j_b + m} b_5^{+ j_b - m} \] (32)
With equations (17, 18) their matrix elements are
\[ \langle \{N_0 0\} J_b m''|\{m'_4 - m_4\} B^{(j_b)}_m|\{N_0 0\} J_b m'\rangle = (2J_b + 1)^{-\frac{1}{2}} \times F_{m m'}^{m'} \langle \{N_0 0\} J_b*|\{m'_4 - m_4\} B^{(j_b)}_m|\{N_0 0\} J_b \rangle \times \left( \frac{[N_b 0] J_b}{[m'_4 - m_4] B^{(j_b)}_m}\right), \] (33)
with for the rmn
\[ \langle \{N_0 0\} J_b|\{m'_4 - m_4\} B^{(j_b)}_m|\{N_0 0\} J_b \rangle = \left( \frac{i^{j_b}}{N_b - m_4} \right) \times \left( \frac{(2J_b + 1)(N_b + j_b + 1)! (N_b - j_b)!}{(m_4 + j_b + 1)! (m_4 - j_b)!} \right)^{1/2}. \] (34)

3.1.2. Symmetrization in \( C_{2v} \)

For the \( \nu_2 \) mode with \( A_1 \) symmetry there is a priori no difficulty. All operators \([m'_4 - m_4] B^{(j_b)}_m \) are of \( A_1 \) species as well as any linear combination
\[ [m'_4 - m_4] B^{(j_b)}_r A_1 = \sum_m [m'_4 - m_4] G^m_{r A_1} \{m'_4 - m_4\} B^{(j_b)}_m, \] (35)
where \([m'_4 - m_4] G \) is a unitary matrix and \( r = 1, \ldots, 2j_b + 1 \) a multiplicity index. However a consistent tensor formalism imposes some restrictions upon the \( G \) matrix.

The matrices for the irrep of \( C_{2v} \), which reduce to characters, being real, the metric tensor may be chosen (and is usually chosen) identical to the identity. This traduces by:
\[ T^\dagger (T) = T (T)^\dagger, \]
for any symmetrized operator, and in particular for the elementary ones
\[ b^{(A_1)} = b^{(A_1)} = b^{+ (A_1)}. \]

For our problem we will not undertake a general discussion as was made for \( E \) modes (24). For \( \nu_2 \) we only need the similarity transformations \([N_0 0] G \) for the states and \([m'_4 - m_4] G \) for the operators. Also from the expression (31) for \([m'_4 - m_4] G_{j_b} (N_4 + N_5) \), with \( A_1 \) symmetry and invariant upon time reversal, we see that we only need to determine \([m'_4 - m_4] G \) for the operators \([m'_4 - m_4] B^{(j_b)}_m (j_b = m_4) \). That is (equation (30)):
\[ [m'_4 - m_4] B^{(j_b)}_r A_1 = \sum_m [m'_4 - m_4] G^m_{r A_1} \{m'_4 - m_4\} B^{(j_b)}_m. \] (36)

- Symmetrized states. From equations (9, 10) we have
\[ \mathcal{K}_e [\{N_0 0\} J_b m]\rangle \equiv \mathcal{K}_e [\{N_0 0\} B^{(j_b)}_m \mathcal{K}_t^{-1} \mathcal{K}_e |0, 0\rangle = (-1)^{N_b} [\{N_0 0\} J_b m]\rangle. \] (37)

If we set
\[ [\{N_0 0\} J_b r A_1]\rangle = e^{i\theta} [\{N_0 0\} J_b m]\rangle, \]
we get symmetrized states invariant upon time reversal if \( e^{2i\theta} = (-1)^{N_b} = i^{2N_b} \), thus a possible choice is:
\[ [\{N_0 0\} J_b r A_1]\rangle \equiv [\{N_0 0\} J_b m A_1]\rangle = i^{N_b} [\{N_0 0\} J_b m]\rangle \equiv (-1)^{j_b - m} m_4 = J_b - m, n_5 = J_b + m >, \] (38)
which amounts to choose
\[ [m_0 0] G^m_{r A_1} = i^{m_4} \delta_{r, m}. \] (39)

- Symmetrized operators. Likewise from the properties (15, 16) under hermitian conjugation and time reversal of the standard tensors, it may be shown that we may built the hermitian symmetrized operators
\[ [m'_4 - m_4] B^{(j_b)}_m |m\rangle_{A_1} = \frac{\varepsilon}{\sqrt{2}} \left( [m'_4 - m_4] B^{(j_b)}_m \right) + (-1)^{j_b - m} [m'_4 - m_4] B^{(j_b)}_{-m}, \] (40)
with \( \varepsilon = 0, 1 \). Operators characterized by \( \varepsilon = 0 \) are invariant upon time reversal (resp. non invariant upon time reversal) \( j_b \) even (resp. \( j_b \) odd); it is the reverse for those characterized by \( \varepsilon = 1 \). Operators “diagonal in \( \nu_2 \)” \([m'_4 - m_4] B^{(j_b)}_0 \) are all invariant upon time reversal. We may thus write an effective bending Hamiltonian:
\[ \mathcal{H}_B = \sum_{m_4 = 0}^{N_b} \sum_{j_b = 0}^{m_4} \{m'_4 - m_4\} \langle j_b |m'_4 - m_4\rangle B^{(j_b)}_0 A_1. \] (41)

- Matrix elements in the symmetrized basis. Several methods can be used for their computation. The simplest is to
use the general formalism, that is to perform the change of
basis associated with the symmetrization process of states
and operators in equation (33). For the general operators
we obtain
\[
\langle [\langle [N_b \rangle J_b] m' A_1] | m A_1, \langle [N_b \rangle J_b] J \rangle = (2J_b + 1)^{-\frac{1}{2}} F^r A_1 \langle [m' A_1] | m A_1, \langle [N_b \rangle J_b] J \rangle = (2J_b + 1)^{-\frac{1}{2}} F^r A_1 \times \left( \langle [N_b \rangle J_b] | m A_1 \right) \| \| J \rangle .
\]
where the last equality follows from (39). The analytical
expressions for these coefficients together with those of the
various matrix elements are given in Appendix A.

3.2. Stretching modes \( \nu_1, \nu_3 \)

3.2.1. Standard states and operators

For the \( su(2) \) Schwiniger’s realization we take:
\[
^{(s)} J_+ = b^+_1 b_2 \quad , \quad ^{(s)} J_- = b^+_2 b_1 \quad , \quad ^{(s)} J_z = \frac{1}{2} (N_1 - N_2) = \frac{1}{2} (b^+_1 b_1 - b^+_2 b_2)
\]
where the indices \( i = 1, 2 \) are linked to the two bonds.

With regard to the notations of section 2.2 we make the
substitutions \( N \rightarrow N_a \), \( j \rightarrow j_s \) for the states and \( T \rightarrow S \)
for the operators. We have then with (30) \( (j_s = n_s/2) \):
\[
\langle [N_a \rangle [n_s \rangle j_s m) | m \rangle = \sum [n_s \rangle 0 - n_s \rangle [n_s \rangle 0 | j_s \rangle [N_a \rangle [00) | 00),
\]
with
\[
\langle [N_a \rangle [00) | 00) \rangle \equiv [00), (N_a) = (N_a!)^{-1/2} b_3^+ N | 00, 0).
\]

We may also express these states in various forms replacing
the \( S \) operator in (15):
\[
\langle [N_a \rangle [n_s \rangle j_s m) | m \rangle = (n_s!)^{1/2} g(n_s, n_s, 0) | [n_s \rangle 0 | j_s \rangle m) | N_s \rangle
\]
\[
= (n_s!)^{1/2} g(n_s, n_s, 0) | [n_s \rangle 0 | j_s \rangle m) | N_s \rangle
\]
\[
= (-1)^{\frac{n_s + m}{2}} m | j_s - m, j_s + m, N_s - n_s). \quad (46)
\]

We thus have the correspondence:
\[
\frac{n_s}{2} - m = n_1 \quad , \quad \frac{n_s}{2} + m = n_2 \quad , \quad N_s - n_s = n_3. \quad (47)
\]

Arbitrary vibrational operators in the algebraic standard
\( u(3) \supseteq u(2) \supseteq su(2) \supseteq so(2) \) chain are obtained from re-
lations (22) (23) and the results for the covariant operators
\( [m_1 - m_2] T(m) \). All their matrix elements are given by equa-
tions (24) (28). In particular, operators which are “diagonal
in \( n_s \)” are characterized by \( m_1 = m_2 \).

3.2.2. Symmetrization in \( C_{2v} \)

The computations have been made with the conventions
given in Table 1. The indices \( i = 1, 2 \) being associ-
ated with the two bonds we have:
\[
P_{C_2} b_1 P_{C_2}^{-1} = b_2 \quad ; \quad P_{s} b_1 P_{s}^{-1} = b_2 \quad ; \quad P_{s} b_1 P_{s}^{-1} = b_i,
\]
where we set \( \sigma = \sigma_{v}(y) \) and \( \sigma' = \sigma_{v}(x) \). Hence the set
\( (b_1, b_2) \) (or \( (b_1^+, b_2^+) \)) span a representation \( A_1 + B_1 \) of \( C_{2v} \).

| \( C_{2v} \) | \( E \) | \( C_{2v}(Oz) \) | \( \sigma_{v}(xz) \) | \( \sigma_{v}(yz) \) |
|---|---|---|---|
| \( A_1 \) | 1 | 1 | 1 | 1 |
| \( A_2 \) | 1 | 1 | -1 | -1 |
| \( B_1 \) | 1 | -1 | 1 | -1 |
| \( B_2 \) | 1 | -1 | -1 | 1 |
\[ P_R (m_1 - m_2) S_{(j)}^m P_R^{-1} = (-1)^{m_1} (m_1 - m_2) S_{(j)}^m, \]  

where \( R = C_2, \sigma \); they are obviously invariant with respect to \( \sigma' \). We may thus build the symmetry adapted tensors \((m > 0)\)

\[ [m_1 - m_2] S_{(j)}^m = \frac{\theta(m_1, m_2, |m|, \Gamma)}{\sqrt{2}} [m_1 - m_2] S_{(j)}^m + (-1)^{m_1 + |m|} [m_1 - m_2] S_{(-m)}^m, \]  

with \( \varepsilon = 0 \) for \( \Gamma = A_1 \) and \( \varepsilon = 1 \) for \( \Gamma = B_1 \). For \( m = 0 \) we simply have

\[ [m_1 - m_2] S_{(j)}^m = \theta(m_1, 2, 0, \Gamma) [m_1 - m_2] S_{(j)}^0, \]  

with

\[ \Gamma = A_1 \text{ for } m_1 \text{ and } m_2 \text{ even;} \]
\[ \Gamma = B_1 \text{ for } m_1 \text{ and } m_2 \text{ odd.} \]  

In order to obtain a correct description (in terms of allowed symmetries in \( C_{2v} \)) for the states associated with the \textit{irrep} \([N \hat{0}]\) of \( u(3) \), we must impose that \( b_3^+ \) (or \( b_3 \)) belongs to the \( A_1 \) scalar representation of \( C_{2v} \). With these conventions, it appears that the \( G(z, m_1, m_2) \) term, given by (22), is invariant in \( C_{2v} \). Consequently the general operators (23) transform, under the action of the \( C_{2v} \) generators, as the standard operators (relation (49)). This property, allows to symmetrize both type of operators with the same orientation matrix and we set for the \( u(3) \) symmetrized operators:

\[
S \begin{bmatrix} z & 0 & -z \\ m_1 - m_2 \end{bmatrix} (j) = \sum_m [m_1 - m_2] G_{[m_1]}^m S \begin{bmatrix} z & 0 & -z \\ m \end{bmatrix} (j),
\]  

where the sum is limited to the values \( m = \pm |m| \) \((m \neq 0)\). The choices for the phase factors have been made so that the operators (53) satisfy:

\[
S \begin{bmatrix} z & 0 & -z \\ m_1 - m_2 \end{bmatrix} (j) = \sum_m [m_2 - m_1] G_{[m]}^m S \begin{bmatrix} z & 0 & -z \\ m \end{bmatrix} (j).
\]  

Under time reversal they are unchanged when \( m_1 \) or \( m_2 \) are zero and multiplied by \((-1)^{j+|m|+\varepsilon}\) when \( m_1, m_2 \neq 0 \). This leads to

\[
[m_1 - m_2] G_{[m]}^m = \frac{1}{\sqrt{2}} \theta(m_1, m_2, |m|, \Gamma), m > 0
\]

\[
[m_1 - m_2] G_{[m]}^{-m} = \frac{1}{\sqrt{2}} \theta(m_1, m_2, |m|, \Gamma)(-1)^{m_1 + \varepsilon}
\]

\[
[m_1 - m_2] G_{[0]}^0 = \theta(m_1, m_2, 0, \Gamma), m = 0
\]

with

\[
\theta(m_1, m_2, |m|, \Gamma) = i^{m_1} i^{j+|m|+\varepsilon} \text{ for } m_1, m_2 \neq 0
\]

\[
\theta(m_1, 0, |m|, \Gamma) = i^{m_1}
\]

\[
\theta(0, m_2, |m|, \Gamma) = i^{m_2} (-1)^{|m|+\varepsilon}.
\]

With the results in this section, keeping terms which are diagonal in \( n_s \) only, we may write the effective stretching Hamiltonian:

\[
\mathcal{H}_S = \sum_{z=0}^{N_z} \sum_{m_1=0}^{N_{m_1}} \sum_{|m_s|} [\Sigma^s] \sum_{[m_s]} \sum_{A_1} \sum_{[m_s]} S \begin{bmatrix} z & 0 & -z \\ m_1 - m_2 \end{bmatrix} (j_s),
\]

with \( j_s = m_1 \) and where the sum \( \Sigma^s \) is over \( |m_s| \) values such that \( j_s + |m_s| = m_1 + |m_s| \) be even.

\bullet Symmetrized states. These are obtained with equations (43, 44, 45, 53):

\[
[N_s \hat{0} | n_s 0 | j_s | m | \Gamma) = S \begin{bmatrix} n_s & 0 & -n_s \\ |m| \end{bmatrix} \left[ |n_s 0 \rangle \langle j_s | \right] |[N_s \hat{0} | 00 0 \rangle ,
\]

with \([n_s 0] G\) obtained from (55, 56). Explicitly we have for the various types of local states:

\textit{Local states} \{(n_1, n_2) \ n_1 = n_2\},
They are associated with $m = 0$ (Eq. 47) which implies $j_\epsilon$ integer or (as $j_\epsilon = n_\epsilon / 2$) $n_\epsilon$ even.

$$[[N_\epsilon \hat{0} [n_\epsilon 0] j_\epsilon 0 A_1]] = (-1)^{n_\epsilon} \frac{n_\epsilon}{2} (n_\epsilon / 2, N_\epsilon - n_\epsilon).$$

(59)

Local states $\{n_1, n_2\}$ $n_1 \neq n_2$.

We have then $|m| \neq 0$ and still setting $\epsilon = 0$ for $\Gamma = A_1$ and $\epsilon = 1$ for $\Gamma = B_1$:

$$[[N_\epsilon \hat{0} [n_\epsilon 0] j_\epsilon m |m\Gamma]] =$$

$$\begin{align*}
&\left(-1\right)^{\frac{n_\epsilon - m}{2}} \sqrt{2} \frac{m - n_\epsilon / 2 + m, N_\epsilon - n_\epsilon} \frac{m - n_\epsilon}{2} + m, N_\epsilon - n_\epsilon).
\end{align*}$$

(60)

With our phase convention they are all invariant under time reversal.

- Matrix elements in the symmetrized basis. They are obtained with a method similar to that used for the bending mode. From equation (24) the transformation to symmetrized states and operators gives

$$\langle \langle \Psi''| \hat{S} |m_1 - m_2] (j) |m\Gamma\rangle\rangle = (2j'' + 1)^{-1/2}$$

$$\times F |m\Gamma] |m'\Gamma'\rangle \langle [n_\epsilon 0] j_\epsilon''|m''\Gamma''\rangle$$

$$\times \sum_{m, m', m''} |m_1 - m_2] |n_\epsilon 0\rangle |j_\epsilon''|m''\rangle$$

$$\times F |m_1 - m_2] j |n_\epsilon 0\rangle |j_\epsilon''|m''\rangle,$$

(61)

where we set $\langle \Psi\rangle = [[N_\epsilon \hat{0} [n_\epsilon 0] j_\epsilon m |m\Gamma]]$ and the rme are given by (28) with the appropriate label substitutions. The symmetry adapted CG coefficients are obtained with

$$F |m\Gamma] |m'\Gamma'\rangle \langle [n_\epsilon 0] j_\epsilon''|m''\Gamma''\rangle$$

$$\times \sum_{m, m', m''} |m_1 - m_2] |n_\epsilon 0\rangle |j_\epsilon''|m''\rangle$$

$$\times F |m_1 - m_2] j |n_\epsilon 0\rangle |j_\epsilon''|m''\rangle.$$

(62)

with $j = (m_1 + m_2) / 2$, $j'' = n_\epsilon / 2$ and $j'' = n_\epsilon / 2$. Also it is important to note that these coefficients are a priori defined only for $n_\epsilon = n_\epsilon + m_1 - m_2$. The matrices $|m_1 - m_2] G$ and $|n_\epsilon 0\rangle G$ are given by equations (55) and (56). The analytical expressions for these coefficients are given in Appendix B.

### 3.3. Stretch-bend interactions

Results in sections 3.1 et 3.2 determine all operators adapted to the study of isolated bending and stretching modes and which may appear in the Hamiltonian or transition moments. Taking into account stretch-bend interactions introduces coupling operators which may be formally written

$$\mathcal{O}_{sb}^{(\Gamma, A_1)} = [\mathcal{S}(\Gamma) \times \mathcal{B}(\Gamma)]^{(\Gamma, A_1)}.$$ 

For our problem $\Gamma_b = A_1$ and the CG for the $C_{2v}$ group are trivial ; we thus simply have

$$\mathcal{O}_{sb}^{(\Gamma, A_1)} = \mathcal{S}(\Gamma) \mathcal{B}(\Gamma),$$

(63)

with $\Gamma_b = A_1$ for Hamiltonian terms. The operators (63) may be written in various manners depending on the case and also depending on what we mean to represent, for instance operators in the untransformed Hamiltonian or effective ones.

#### 3.3.1. Method in the case of a polyad structure

The chosen dynamical algebra assumes $\omega_1 \approx \omega_2 \approx \omega_3$ and we have to take into account in the effective Hamiltonian the resonance with the bending mode which determines the polyad structure. We assume

$$\omega_1 \approx \omega_2 = \omega_3 \approx \kappa = \kappa \omega_b.$$

Within our formalism the operator $N_1 + N_2 = n_s$, with eigenvalue $n_s$, represents the “number of quanta of stretching” operator ; $N_4$ with eigenvalue $n_4 = n_b$ the “number of quanta of bending” operator with

$$N_4 \equiv N_b = \frac{N_4 + N_5}{2} + \frac{N_4 - N_5}{2} = \frac{N_b}{2} + (b) J_z.$$

(64)

To a given $P$ polyad we may associate the $\hat{P}$ operator

$$\hat{P} = \hat{n}_b + \kappa \hat{n}_s = N_4 + k (N_1 + N_2),$$

(65)

which may be expressed in terms of the ITO defined previously knowing that:

$$N_4 = \sqrt{2} (\hat{I}_0) \hat{S}(A_1) + [\hat{I}_0] \hat{B}(A_1).$$
\[ N_1 + N_2 = \frac{2}{3} \left( N_s - \sqrt{\frac{3N_s}{2}} \right) \begin{bmatrix} 1 & 0 & -1 \\ 0 & 0 & 0 \\ 0 & A_1 \end{bmatrix} \]

An \( O \) operator which conserves the \( P \) quantum number associated with a given polad must satisfy the condition \([K,O] = 0\), be of species \( A_1 \) and invariant upon time reversal if it belongs to the Hamiltonian expansion. To determine the possible \( O \) operators it appears that it is better to work first in the standard algebraic chain

\[
u(3)_S \otimes u(2)_B \supset u(2)_S \otimes u(2)_B \supset [N_s \hat{0}] [N_b 0] [n_s 0] [N_b 0]
\]

\[ su(2)_S \otimes su(2)_B \supset so(2)_S \otimes so(2)_B \]

\[ j_s = n_s/2 \quad j_b = N_b/2 \quad m_s \quad m_b \]

where the indicated symmetries are those of the states. We thus start from the operator basis

\[ SB = S \begin{bmatrix} z & 0 & -z \\ [m_1 - m_2] (j_s) & [m_4 - m_4] B^{(j_b)}_{m_b} \end{bmatrix} \]

with \( j_b = m'_4 \) and \( j_s = (m_1 + m_2)/2 \). A straightforward calculation gives

\[ [\hat{P},SB] = [-m_b + k(m_1 - m_2)]SB, \]

thus the condition \([\hat{P},SB] = 0\) is satisfied if

\[ m_b = k(m_1 - m_2), \]

with \( k = 2 \) for the considered \( XY_2 \) molecules. This condition being independent of \( m_s \), it appears that, in order to determine hermitian interaction operators having also a determined behavior upon time reversal, it is preferable to keep the standard form for the bending operators and to take symmetrized operators for the stretching ones. We mainly have two cases:

- \( m_b = 0 \) then \( m_1 = m_2 \)

In this case we can also take directly symmetrized bending operators, which gives the hermitian operators

\[ O_{sb}(1) = S \begin{bmatrix} z & 0 & -z \\ [m_1 - m_1] (j_s) & [m_4 - m_4] B^{(j_b)}_{0A_1} \end{bmatrix}, \]

satisfying upon time reversal (see sections \[3.3.2\])

\[ \mathcal{K}O_{sb}(1)\mathcal{K}^{-1} = (-1)^{m_1 + |m_s| + \varepsilon} O_{sb}(1). \]

- \( m_b \neq 0 \)

\[ \text{From the set } \{66\} \text{ we may build the hermitian operators (equations } \{15\}, \{54\}) \]

\[ O_{sb}(2) = \frac{i\tau}{\sqrt{2}} \begin{bmatrix} z & 0 & -z \\ [m_1 - m_2] (j_s) & [m_4 - m_4] B^{(j_b)}_{m_b} \end{bmatrix} \]

\[ + (-1)^\tau(-1)^{j_b + m_b} S \begin{bmatrix} z & 0 & -z \\ [m_2 - m_1] (j_s) & [m_4 - m_4] B^{(j_b)}_{-m_b} \end{bmatrix} \]

with \( \tau = 0, 1 \) and where \( m_b > 0 \) and \( m_1 > m_2 \) is assumed. With the properties established in sections \([3.3.2]\) one shows that

\[ \mathcal{K}O_{sb}(2)\mathcal{K}^{-1} = \begin{cases} (-1)^\tau(-1)^{j_b} (-1)^{\varepsilon + |m_s|} O_{sb}(2) & (a) \\ (-1)^\tau(-1)^{j_b} O_{sb}(2) & (b) \end{cases} \]

where case (a) (resp. (b)) is for \( m_2 
eq 0 \) (resp. \( m_2 = 0 \)).

3.3.2. First operators in the Hamiltonian for \( k = 2 \)

Since the operators \( B \) only differ from the \( B \) ones through a constant function within the \( irrep [N_b 0] \), we can make in equations \([68, 69]\) the substitutions

\[ [m_4 - m_4] B^{(j_b)}_{m_b} \rightarrow [m'_4 - m'_4] B^{(j_b)}_{m_b} \quad (j_b = m'_4), \]

to define the terms (and the parameters) of the effective Hamiltonian.

- For \( m_b = 0 \) (and \( m_4 \neq 0, z \neq 0 \)) the operators \([65] \), with \( \Gamma_s = A_1 \) and \((-1)^{m_1 + |m_s| + \varepsilon} = 1\) are products of operators belonging to \( \mathcal{H}_B \) and \( \mathcal{H}_s \).

- The cases \( m_b \neq 0 \) correspond to non trivial (that is non diagonal) interaction operators. With \( k = 2 \) and as
4. Application to \(D_2S\)

4.1. Effective stretching Hamiltonian

Up to the second order, that is for \(z \leq 2\), the general expansion \([67]\) involves terms with the following values for the labels:

\[
\begin{align*}
\text{for } & z = 0 \quad m_1 = 0, \quad j_s = 0 \quad |m_s| = 0 \\
\text{for } & z = 1 \quad m_1 = 0, \quad j_s = 0 \quad |m_s| = 0 \\
\text{for } & m_1 = 1, \quad j_s = 1 \quad |m_s| = 1 \\
\text{for } & m_1 = 2, \quad j_s = 2 \quad |m_s| = 0 \\
\end{align*}
\]

With the results of sections 2.2.1 and 3.2.2, \(H_S\) can be written in terms of elementary boson operators as

\[
H_S = \left\{ (0)^i_{t_0} + \frac{(1)^i_{t_0}}{2} \sqrt{\frac{2}{3N_s}} [N_3 - \frac{1}{2}(N_1 + N_2)] \right\} + \left\{ (1)^{\bar{i}}_{\bar{t}} + \frac{(2)^{\bar{i}}_{\bar{t}}}{\sqrt{2N_s}} \right\},
\]

with \(\alpha_{2,N_s} = [2N_S(N_S - 1)]^{-\frac{1}{2}}\).

For the fitting procedure, it can be rewritten to the more convenient form:

\[
H_S = \alpha_0 (N_1 + N_2) + \alpha_1 (N_1^2 + N_2^2) + \alpha_2 N_1 N_2 + \alpha_3 \lambda \langle A_1 \rangle + \alpha_4 (N_1 + N_2) \lambda \langle A_1 \rangle + \alpha_5 [\lambda \langle A_1 \rangle \times \lambda \langle A_1 \rangle] \langle A_1 \rangle,
\]

where \(\lambda \langle A_1 \rangle = b_1^+ b_2 + b_2^+ b_1\) and where we removed the part of \(H_S\) which depends upon the operator \(N_s\) only since the latter takes a constant value within the irrep \([N \bar{0}]\) of \(u(3)\). Also we set:

\[
\begin{align*}
\alpha_0 &= -\frac{(1)^i_{t_0} + \frac{(2)^{\bar{i}}_{\bar{t}}}{\sqrt{2N_s}}}{\sqrt{2N_s}} + \frac{(2)^i_{t_0} (1 - 6N_s)}{\sqrt{2N_s}}, \\
\alpha_1 &= \alpha_{2,N_s} \left[ (2)^i_{t_0} \sqrt{\frac{2}{3}} \lambda \langle A_1 \rangle + \frac{(2)^{\bar{i}}_{\bar{t}}}{\sqrt{2N_s}} \right], \\
\alpha_2 &= \alpha_{2,N_s} \left[ (2)^i_{t_0} \sqrt{\frac{2}{3}} \lambda \langle A_1 \rangle - \frac{(2)^{\bar{i}}_{\bar{t}}}{\sqrt{2N_s}} \right], \\
\alpha_3 &= \frac{1}{\sqrt{2N_s}} + \frac{(2)^i_{t_0}}{\sqrt{2N_s}} \alpha_{2,N_s}, \\
\alpha_4 &= -\frac{(2)^i_{t_0}}{\sqrt{2N_s}} \alpha_{2,N_s}. \\
\end{align*}
\]
4.2. Effective bending Hamiltonian

The general expression may also be written, using the results in section (31.1.2):

$$H_B = \sum_{m_4=0}^{N_b} \sum_{m_4} \{m_4\} t^{(j_b)} [m_4' - m_4'] g^{(j_b)}_{m_4} (N_4 + N_5) B_{0,A_1}^{(j_b)},$$

with $j_b = m_4'$ and $\{m_4,m_4\} g^{(j_b)}_{m_4}$ defined in (31). As a given $j_b$ (or $m_4'$) value appears for all $m_4 \geq j_b$ values and since $N_4 + N_5$ takes a constant $N_b$ value within the irrep $[N_b,0]$ of $u(2)_B$ we may set

$$H_B = \sum_{j_b=0}^{N_b} \{t^{(j_b)} [m_4' - m_4'] B_{0,A_1}^{(j_b)},$$

with the effective parameters:

$$\tilde{t}^{(j_b)} = \sum_{m_4=m_4}^{N_b} \{m_4\} t^{(j_b)} [m_4,m_4] g^{(j_b)}_{m_4} (N_b).$$

For instance up to second order we have:

$$H_B^{(2)} = \tilde{t}^{(0)} + \tilde{t}^{(2)} [1 - 2 - 2] B_{0,A_1}^{(2)},$$

$$= \tilde{t}^{(0)} + \frac{\tilde{t}^{(2)} (N_4 - N_5)}{2} + \frac{\tilde{t}^{(2)}}{2 \sqrt{6}} \left[ b_1^2 b_3^2 + b_5^2 b_3^2 - 4 b_1^2 b_5^2 b_4 b_5 \right],$$

$$= \beta_0 N_4 + \beta_1 N_4^2$$

where the last form has a clearer physical meaning, with parameters $\beta_0$, $\beta_1$ given by:

$$\beta_0 = \sqrt{2} \tilde{t}^{(1)} = \sqrt{3} \frac{N_b \tilde{t}^{(2)}}{2}, \quad \beta_1 = \sqrt{3} \frac{\tilde{t}^{(2)}}{2}.$$

4.3. Effective stretch-bend interaction operators

As noted before these interaction operators may be divided in two groups. In the first one we have products of stretching and bending operators diagonal with respect to $n_s$ and $n_b$. In the second one are those obtained from the properties of the $u(3)_S$ and $u(2)_B$ dynamical algebras and which take into account the approximate resonance between the stretching an bending modes. Keeping only operators of lowest degree the stretch-bend effective Hamiltonian can be expressed as (equations (68), (70)):

$$H_{SB}^{I} = \gamma_0 (N_1 + N_2) N_4 + \gamma_1 N_1 Y^{(A_1)},$$

$$\mathcal{H}_{SB}^{II} = \gamma_2 (b_1^2 b_3^2 b_4^2 + b_1^2 b_3^2 b_4^2 + \text{h.c.}) = \gamma_2 O_{SB}^{II}.\quad (80)$$

It is worth to analyze more deeply this last operator which indeed traduces the resonance $\nu_1 (A_1) \approx \nu_3 (B_1) \approx 2 \nu_2 (A_1)$. Thus the Hamiltonian matrix, already divided into two $A_1$ and $B_1$ blocks, is subdivided into sub-blocks characterized by the polyad number $P = 2(n_1 + n_2) + n_b$. Within each $P$-block, $H_{SB}^{II}$ connects states which are not diagonal neither in $n_s$ nor in $n_b$.

$O_{SB}^{II}$ can also be written $(b_1^2 + b_3^2) b_4^2 (b_5^2 + b_3^2) + \text{h.c.}$. In this form it is clear that the dependence of its matrix elements upon the quantum numbers $n_1$, $n_2$ and $n_b$ are similar to that of a usual Fermi interaction operator. However contrarily to the later, which leads to convergence problems for high values of the quantum numbers, the other factor the matrix elements of which behave roughly as $(N_s - n_s)^{1/2} (N_b - n_b)$, has a damping effect as $n_s$ and (or) $n_b$ increase ($N_s$ and $N_b$ fixed).

We already defined a similar operator adapted to $XY_3$ pyramidal molecules in (34, 35) and already proved that this operator does not require the knowledge of $N_s$ and $N_b$ for low values of the quantum numbers $n_1$, $n_2$ and $n_3$ as it physically must be near the minimum of the potential function.

4.4. Numerical application

To illustrate the efficiency of our formalism, we apply it to the deuterate hydrogen sulfide. The hydrogen sulfide molecule and its isotopic species are of interest for terrestrial atmospheric pollutant measurements. They are involved in the study of planet atmospheres and appear in the analysis of interstellar medium. Also, hydrogen sulfide is a good candidate to apply local mode models. We restrict here to the $D_2S$ molecule but will present a comparative analysis with other $XY_2$ molecules in a next paper. Renaming, for simplicity, the parameters $a_i$ (i=0, ...,7),
the best fitted Hamiltonian is defined as follows:

\[ H = a_0(N_1 + N_2) + a_1(N_1^2 + N_2^2) + a_2N_1N_2 + a_3Y^{(A_1)} + a_4N_4 + a_5 N_4^2 + a_6 O_{SB}^{II} + a_7(N_1 + N_2)N_4. \]  

(81)

However, taking into account the \( N_s \) and \( N_b \) quantum numbers, there are 10 parameters to determine in our model since the value of these numbers appears explicitly in the matrix elements of \( O_{SB}^{II} \). To obtain the optimum values of these quantum numbers, we simply operate as follows. An initial set for the parameters \( a_i^{(0)} \) \( (i = 0, 1, 4, 5) \) is obtained from the experimental values of the lowest vibrational bands. This allows to have approximate values for the stretching levels when \( n_s \) quanta are localized on one bond and for the bending levels:

\[ E_s^{(0)}(n_s) = a_0^{(0)} n_s + a_1^{(0)} n_s^2, \quad E_b^{(0)}(n_b) = a_4^{(0)} n_b + a_5^{(0)} n_b^2. \]

As for any anharmonic potential (Morse or modified Pösch-Teller for instance) the \( n_{\text{max}} \) value of the vibrational quantum number is given by the extremum of the \( E_s^{(0)}(n_s) \) and \( E_b^{(0)}(n_b) \) curves. With

\[ a_0^{(0)} = 1927.5855 \text{ cm}^{-1}, \quad a_1^{(0)} = -24.4279 \text{ cm}^{-1}, \quad a_4^{(0)} = 858.2604 \text{ cm}^{-1}, \quad a_5^{(0)} = -2.8564 \text{ cm}^{-1}, \]

we obtained in this way:

\[ n_{s, \text{max}} = -\frac{a_0^{(0)}}{2a_1^{(0)}} = 39.45, \quad n_{b, \text{max}} = -\frac{a_4^{(0)}}{2a_5^{(0)}} = 150.23, \]

hence we could take \( (N_s^{(0)}, N_b^{(0)}) = (39, 150) \). However this high value for \( N_b^{(0)} \) is not reasonable for the following reasons. As it is commonly accepted \( N_s \) may be interpreted as the number of excitation quanta which, when concentrated on one bond, may dissociate the molecule. Within a polyad \( P \) to which a \( |N_s, 0, 0 \rangle \) stretching state belongs, we also have states \( |0, 0, N_s\rangle \) \( (2N_s, N_b - 2N_s) \) which implies that \( N_b \geq 2N_s \), but on the other hand if we took \( N_b^{(0)} \) much greater than \( 2N_s^{(0)} \), we would have many dissociating states within polyads with \( P \geq 2N_s^{(0)} \). It would be quite unrealistic to pretend that our model is capable to reproduce isolated stable states within the continuum.

Another method to obtain a reasonable value for \( N_s^{(0)} \) is to use for \( E_s^{(0)}(n_s) \) the known experimental value of the dissociation energy \( 36 \):

\[ a_0^{(0)} n_s + a_1^{(0)} n_s^2 \approx 32050 \pm 50 \text{ cm}^{-1}, \]

which leads to \( N_s^{(0)} = 24 \). Various fits were performed starting thus with \( (N_s^{(0)}, N_b^{(0)}) = (39, 78) \) while the other \( a_i \) \( (i = 0, \cdots, 7) \) parameters were determined through a usual non-linear least square fit method. We noticed that, except for the \( a_6 \) parameter associated with \( O_{SB}^{II} \) the matrix elements of which depend strongly upon the \( N_s \) and \( N_b \) values, other parameters remained almost unchanged (less than some percent of relative variation) while \( N_s \) and \( N_b \) decreased. One of the indicators of the convergence of the fitting process was the minimization of the standard deviation

\[ \sigma(d, p) = \sqrt{\frac{1}{d-p} \sum_{i=1}^{d} \left( \frac{E_i^{(\text{cal})} - E_i^{(\text{obs})}}{\sigma_i} \right)^2}, \]

where \( d \) and \( p \) are respectively the number of experimental data and the number of parameters included in the fit.

It soon appeared that this indicator was rather insensitive to the \( N_b \) value in a rather large range. A similar effect was already noticed in previous studies of pyramidal molecules \[35\]. On the other hand using the initial \( (N_s^{(0)}, N_b^{(0)}) = (24, 48) \) values improved drastically the convergence to the minimum value \( \sigma(22, 8) = 0.514 \text{ cm}^{-1} \), thus reducing noticeably the computational time. The second indicator is, of course, the parameters stability at the end of the fitting procedure; the last variation \( \Delta a_i \) of the parameters fulfilled the condition \( |\Delta a_i/a_i| < 10^{-7} \), \( (0 \leq i \leq 7) \). The retained Hamiltonian \[31\] led to the set of parameters given in Table\[2\] (these are given with values in parentheses which are \( 1 \sigma \) statistical confidence intervals in units of the last digits).

Finally we compared the experimental dissociation energy with the value calculated from our model. This was done in two ways. First, removing all off-diagonal terms in the Hamiltonian \[31\], the energy of the \( |24, 0, 0 A_1 \rangle \) (or
Table 2: Parameters (in cm$^{-1}$) fitted with 22 experimental data.

| $a_0$   | 1927.908(290) |
|---------|---------------|
| $a_1$   | -24.665(103)  |
| $a_2$   | -0.845(288)   |
| $a_3$   | -6.428(140)   |
| $a_4$   | 858.821(447)  |
| $a_5$   | -3.103(141)   |
| $a_6$   | 0.005(001)    |
| $a_7$   | -10.488(150)  |

|24, 0, 0 $A_1$) pure stretching state is computed with the $a_0$ and $a_1$ parameters of Table 2 which leads to the dissociation energy $E_D = 32063$ cm$^{-1}$, or more precisely if we take into account the parameter uncertainties $31996$ cm$^{-1} < E_D < 32129$ cm$^{-1}$. The second way to calculate $E_D$ is to diagonalize the Hamiltonian [51] within the $P = 48$ polyad with the parameters $a_i$ (i=0, ...,7) of Table 2. The value obtained for the [24, 0, 0 $A_1$], [24, 0, 0 $B_1$] levels is $E_D' = 32062$ cm$^{-1}$ which is 1 cm$^{-1}$ close to the previously calculated $E_D$ value, which confirms the validity of our previous assumption to keep only diagonal operators to evaluate this dissociation energy. Taking again into account the uncertainty on the parameters, we found that the diagonalization of the $P = 48$ Hamiltonian matrix with the two sets:

\[
\{a_i(\text{min})\} = \{a_0^-, a_1^-, a_2^-, a_3^-, a_4^-, a_5^-, a_6^+, a_7^-\}
\]

\[
\{a_i(\text{max})\} = \{a_0^+, a_1^+, a_2^+, a_3^+, a_4^+, a_5^+, a_6^-, a_7^+\},
\]

where $a_i^-$ (resp. $a_i^+$) stands for the lowest (resp. highest) value of the $a_i$ parameter according to the 1σ statistical confidence interval leads to

$E_{D_{\text{min}}} = 31996$ cm$^{-1} < E_D' < E_{D_{\text{max}}} = 32128$ cm$^{-1}$.

Both methods lead to similar values also consistent with the experimental results.

Experimental and calculated energies of $D_2S$ vibrational levels are given in Table 3. The first column gives the normal notation ($\nu_1 \nu_2 \nu_3$) of the level. The second one indicates the polyad $P$ number. The third column indicates the levels in local notation with explicit symmetric (+) and antisymmetric (-) labels. The usual local mode notation has been adapted to our notation as follows $mn^\pm, v \equiv n_1 n_2^\pm, n_4 \equiv n_b$. Column 4 gives the eigenvalues, whereas column 5 indicates the observed energy levels. Column 6 gives the difference Observed-Calculated energy. The last column shows that the eigenkets are close to the initial basis given in columns 1 and 3. We mention that all the experimental data used in the present paper are reported in [14].

5. Conclusion

We developed a formalism which allows a complete description of vibrational modes in local $XY_2$ type molecules. Stretching, bending, interaction and transition operators have been built and analytical expressions for their matrix elements established in the chains $u(2) \supset su(2) \supset so(2)$ and $u(3) \supset u(2) \supset su(2) \supset so(2)$. Next a full symmetry adaptation in the $C_{2v}$ molecular point group has been performed. This formalism has been applied to the $D_2S$ molecule where the 2:1 resonance between stretching and bending modes has been taken into account through an adapted Fermi-type operator the properties of which have been discussed. From a simplified model we derived reasonable values for the highest stretching $N_s$ and bending $N_b$ quantum numbers. Experimental data are reproduced with a standard deviation $\sigma = 0.5$ cm$^{-1}$ and only 8 effective spectroscopic parameters. The dissociation energy calculated with these parameters is in good agree-
ment with the experimental one and this also confirms our method for the determination of the \( N_s \) value. Our approach will be applied to other XYZ molecular systems in a next paper.

6. Acknowledgments

This work was partially supported by a first financial support of the CNRS and the FRBR through a PICS (N° 170908) between the Institut Carnot de Bourgogne - Université de Bourgogne - France and the Laboratory of Molecular Spectroscopy - Tomsk State University - Russia and a second financial support through a grant (YS Fellowship N° 06-1000016-5751) INTAS - Bruxelles - Belgium for Olga Gromova during her stays in the ICB. We want particularly to thank Martine Bonin from INTAS for all her nice helps and excellent explanations.

A. Symmetry adapted Clebsch-Gordan coefficients and matrix elements for \( \nu_2 \)

The expressions for the \([m_1 - m_4]_1 G\) matrix elements are obtained from equations \([56, 40]\) which lead to:

\[
[m_1' - m_4'] G_{0A_1}^{m} = i^{m_4'} \delta_{m,0},
\]

\[
[m_1' - m_4'] G_{m|\varepsilon A_1}^{m} = \frac{i \varepsilon}{\sqrt{2}} \delta_{m,|m|},
\]

\[
[m_1' - m_4'] G_{|m|\varepsilon A_1}^{m} = \frac{i \varepsilon}{\sqrt{2}} (-1)^{1} (1)^{m_4 + m} \delta_{m,|-m|}.
\]

As a result:

• For \( r = 0 \) we obtain the CG \([43]\)

\[
F \begin{pmatrix} 0 A_1 & m' A_1 \\ ([N_0,0] J_0) & m'' A_1 \end{pmatrix} = \begin{pmatrix} [m_4' - m_4'] J_b & [N_0,0] J_b \\ m'' A_1 \end{pmatrix}
\]

\[
= -i^{-m_4'} C \begin{pmatrix} 0 & m' (J_b) \\ (J_b) & m'' \end{pmatrix} = i^{m_4'} \delta_{m',m''},
\]

(A.2)

and for the matrix elements \([42]\):

\[
\langle \langle [N_0,0] J_b | m'' A_1 | m_4' - m_4' [B_{0A_1}^{(j_0)} | [N_0,0] J_b | m' A_1] \rangle \rangle = i^{m_4'} \delta_{m',m''}
\]

\[
\times (2 J_b + 1)^{-\frac{1}{2}} \left( [N_0,0] J_b | [m_4' - m_4'] [B_{0A_1}^{(j_0)} | [N_0,0] J_b \rangle \right),
\]

(A.3)

For \( r = |m| \varepsilon \). With \([A.1]\) we obtain in this case for the CG \([43]\):

\[
F \begin{pmatrix} |m| A_1 & m' A_1 \\ ([N_0,0] J_0) & m'' A_1 \end{pmatrix} = \begin{pmatrix} [m_4' - m_4'] J_b & [N_0,0] J_b \\ m'' A_1 \end{pmatrix}
\]

\[
= (-i)^{r} \frac{1}{\sqrt{2}} \begin{pmatrix} C & m & m' (J_b) \\ (J_b) & m'' \end{pmatrix}
\]

\[
+ (-1)^{r} (1)^{m_4 + m} C \begin{pmatrix} -m & m' (J_b) \\ (J_b) & m'' \end{pmatrix}
\]

This last expression is to be taken with \( m > 0 \) (one can also set \(|m|\) in the CG). We then have for the matrix elements \([42]\):

\[
\langle \langle [N_0,0] J_b | m'' A_1 | m_4' - m_4' [B_{0A_1}^{(j_0)} | [N_0,0] J_b | m' A_1] \rangle \rangle = \begin{pmatrix} 2 J_b + 1 \end{pmatrix}^{-\frac{1}{2}} \frac{i^{r}}{\sqrt{2}} \begin{pmatrix} C & m & m' (J_b) \\ (J_b) & m'' \end{pmatrix}
\]

\[
\times \left( [N_0,0] J_b | [m_4' - m_4'] [B_{0A_1}^{(j_0)} | [N_0,0] J_b \rangle \right),
\]

(A.5)

where we took into account that the \( su(2) \) standard CG are real.

B. Symmetry adapted Clebsch-Gordan coefficients for \( \nu_1, \nu_3 \)

We give below the symmetry adapted CG coefficients used in the study of stretching modes. They are obtained from equations \([55, 56, 62]\). The remaining standard \( su(2) \) coefficients are taken from \([30]\).

• \(|m| = |m'| = |m''| = 0\)

This condition implies \( n_s = 2 j_s', n_s'' = 2 j_s'' \) and \( m_1 + m_2 \)
even. 

\[
F = \begin{pmatrix} 0 \Gamma & 0 \ A_1 \end{pmatrix} ([n^0_s]_{j^s})_{\nu} = \\
( [m_1 - m_2] j \ [n^0_s]_{j^s} )_{\nu} 0 \ A_1 \\
\end{pmatrix}
\]

\[
i^{-m_2 - j} C \begin{pmatrix} 0 & 0 \ (j^\nu) \end{pmatrix}_{\nu} = i^{-j}(n^0_s + m_1 - m_2 + 1)^{\frac{1}{2}}
\]

\[
\times \left[ \left( n^0_s - m_2 \right)! \left( m_1 \right)! \left( m_2 \right)! \right]^{\frac{1}{2}}
\]

\[
\times \left( \frac{(n^0_s + m_1 + 1)!}{(n^0_s - m_2 - 2)! \left( m_1 \right)! \left( m_2 \right)!} \right) \delta_{j^s, \nu}. \] (B.1)

As it is known the CG on the second line in non zero only
if \( j + j^s + j^\nu \) is even which corresponds to the selection rule \( \Gamma = A_1 \).

• \( |m| = |m'| = 0, |m''| \neq 0 \) or \( |m| = |m''| = 0, |m'| \neq 0 \) or
|\( m'| = |m''| = 0, |m| \neq 0 \)

It is easily checked that all \( F \) coefficients are zero in these cases.

• \( |m| = 0, |m'| \neq 0, |m''| \neq 0 \)

\[
F = \begin{pmatrix} 0 \Gamma & |m'|\Gamma' \ (n^0_s]_{j^s})_{\nu} \end{pmatrix} = i^{-m_2} i^{-j - \epsilon}
\]

\[
( [m_1 - m_2] j \ [n^0_s]_{j^s} )_{\nu} |m''|\Gamma''
\]

\[
\times C \begin{pmatrix} 0 & m' \ (j^\nu) \end{pmatrix}_{\nu} \frac{1}{2} \delta_{m'|.,m''}(B.2)
\]

We note that the factor \( 1 + (-1)^{m_1 + \epsilon + \epsilon''} \) just traduces the selection rule \( \Gamma \times \Gamma' = \Gamma'' \). In fact for the CG to be non zero we must have \( (-1)^{m_1 + \epsilon + \epsilon''} = 1 \), that is for \( m_1 \) even \( \Gamma = A_1 \) and \( \epsilon' = \epsilon'' \) that is \( \Gamma' = \Gamma'' \) \( (A_1 \ or \ B_1) \) ; for \( m_1 \) odd, \( \Gamma = B_1 \) and \( \epsilon' \neq \epsilon'' \) that is \( \Gamma' \neq \Gamma'' \) \( ((\Gamma', \Gamma'') = (A_1, B_1) \ or \ (\Gamma', \Gamma'') = (B_1, A_1)) \).

• \( |m'| = 0, |m| \neq 0, |m''| \neq 0 \)

In this case we necessarily have \( j^s \) integer so \( n^0_s \) even and \( \Gamma' = A_1 \). Here again a factor \( 1 + (-1)^{\epsilon + \epsilon''} \) appears in the computation, which is equivalent to \( \Gamma = \Gamma'' \). We find

\[
F = \begin{pmatrix} |m|\Gamma & 0 \ A_1 \end{pmatrix} ([n^0_s]_{j^s})_{\nu} = i^{-m_2} i^{-j - |m| - \epsilon}
\]

\[
( [m_1 - m_2] j \ [n^0_s]_{j^s} )_{\nu} |m''|\Gamma''
\]

\[
\times C \begin{pmatrix} m & 0 \ (j^\nu) \end{pmatrix}_{\nu} \delta_{m'|.,m''} \delta_{\Gamma,\Gamma''}. \] (B.3)

• \( |m'| = 0, |m| \neq 0, |m''| \neq 0 \)

This case is similar to the preceding one. We necessarily have \( j^s \) integer so \( n^0_s \) even and \( \Gamma'' = A_1 \). Here again a factor \( 1 + (-1)^{\epsilon + \epsilon''} \) appears in the computation, which is equivalent to \( \Gamma = \Gamma'' \). We obtain

\[
F = \begin{pmatrix} |m|\Gamma & |m'|\Gamma' \ ([n^0_s]_{j^s})_{\nu} \end{pmatrix} = i^{-m_1} i^{-j - |m| - \epsilon}
\]

\[
( [m_1 - m_2] j \ [n^0_s]_{j^s} )_{\nu} 0 \ A_1
\]

\[
\times C \begin{pmatrix} m & -m \ (j^\nu) \end{pmatrix}_{\nu} \delta_{m',|m''} \delta_{\Gamma,\Gamma'} \] (B.4)

We underline that in equations \( B.2 \ B.3 \ B.4 \) the \( su(2) \) CG in the right member is to be taken with \( m \) (or \( m' \)) positive.

• \( |m'| \neq 0, |m| \neq 0, |m''| \neq 0 \)

In all cases a coefficient \( 1 + (-1)^{\epsilon + \epsilon''} \) appears in the calculation, which traduces the selection rule \( \Gamma'' = \Gamma' \times \Gamma'' \) .

We obtain the following non-zero coefficients:

- For \( |m'| = |m| + |m''| \)

\[
F = \begin{pmatrix} |m|\Gamma & |m'|\Gamma' \ ([n^0_s]_{j^s})_{\nu} \end{pmatrix} = i^{-m_2} i^{-j - |m| - \epsilon}
\]

\[
( [m_1 - m_2] j \ [n^0_s]_{j^s} )_{\nu} |m''|\Gamma''
\]

\[
\times C \begin{pmatrix} m & m' \ (j^\nu) \end{pmatrix}_{\nu} \delta_{m'|.,m''} \delta_{\Gamma,\Gamma''}. \] (B.5)

- For \( m > m' > 0 \)

\[
F = \begin{pmatrix} |m|\Gamma & |m'|\Gamma' \ ([n^0_s]_{j^s})_{\nu} \end{pmatrix} = i^{m'' + \epsilon''} i^{-j - |m| + \epsilon}
\]

\[
( [m_1 - m_2] j \ [n^0_s]_{j^s} )_{\nu} |m''|\Gamma''
\]

\[
\times C \begin{pmatrix} m & -m' \ (j^\nu) \end{pmatrix}_{\nu} \delta_{m'|.,m''} \delta_{\Gamma,\Gamma''}. \] (B.6)

- For \( m' > m > 0 \)

\[
F = \begin{pmatrix} |m|\Gamma & |m'|\Gamma' \ ([n^0_s]_{j^s})_{\nu} \end{pmatrix} = i^{-m_1} i^{-j - |m| + \epsilon}
\]

\[
( [m_1 - m_2] j \ [n^0_s]_{j^s} )_{\nu} |m''|\Gamma''
\]

\[
\times C \begin{pmatrix} m & -m' \ (j^\nu) \end{pmatrix}_{\nu} \delta_{m'|.,m''} \delta_{\Gamma,\Gamma''}. \] (B.7)

References

[1] J. Lamouroux, L. Régalia-Jarlot, V.L.G. Tyuterev, X. Thomas, P. Von der Heyden, S.A. Tashkun, Yu, Borkov, J. Mol. Spectrosc. 250 (2008) 117-125.

[2] Z. Zelinger, A. Perrin, M. Stržižk, P. Kubat, J. Mol. Spectrosc. 249 (2008), 117-120.

[3] T.A. Ford, J. Mol. Struct. 834-836 (2007) 30-41.
Table 3: Observed and calculated energies of $D_2S$ with 22 experimental data. ($1 \leq P \leq 12$).

| Normal | Polyad | Local | $E_{\text{cal}}$ | $E_{\text{obs}}$ | $E_{\text{obs}} - E_{\text{cal.}}$ | $\%\text{init.ket}$ |
|--------|--------|-------|-----------------|-----------------|--------------------------|---------------------|
| $\nu_1$ | $\nu_2$ | $\nu_3$ | $P$ | $n_1n_2 \pm n_4$ | cm$^{-1}$ | cm$^{-1}$ | cm$^{-1}$ | (Modulus) |
| 0 1 0 | $P=1$ | 00$^+$, 1 | 855.71821 | 855.40416 | -0.31405 | 1.00000 |
| 0 2 0 | $P=2$ | 00$^+$, 2 | 1705.19892 | | | |
| 1 0 0 | $P=2$ | 10$^+$, 0 | 1896.84567 | 1896.43154 | -0.41413 | 0.99992 |
| 0 0 1 | $P=2$ | 10$^-$, 0 | 1909.67175 | 1910.18375 | 0.51200 | 1.00000 |
| 0 3 0 | $P=3$ | 00$^+$, 3 | 2548.44694 | 2549.07336 | 0.62642 | 0.99977 |
| 1 1 0 | $P=3$ | 10$^+$, 1 | 2742.13327 | 2742.66570 | 0.53243 | 0.99977 |
| 0 1 1 | $P=3$ | 10$^-$, 1 | 2754.90182 | 2754.45192 | -0.44990 | 1.00000 |
| 0 4 0 | $P=4$ | 00$^+$, 4 | 3385.46874 | | | 0.99958 |
| 1 2 0 | $P=4$ | 10$^+$, 2 | 3583.56418 | | | 0.99941 |
| 0 2 1 | $P=4$ | 10$^-$, 2 | 3593.89050 | 3593.12888 | -0.76162 | 0.99989 |
| 2 0 0 | $P=4$ | 20$^+$, 0 | 3754.01 | 3753.47 | -0.54 | 0.97041 |
| 1 0 1 | $P=4$ | 20$^-$, 0 | 3757.19161 | 3757.45948 | 0.26787 | 0.99989 |
| 0 0 2 | $P=4$ | 11$^+$, 0 | 3808.85313 | 3809.15400 | 0.30087 | 0.97049 |
| 0 5 0 | $P=5$ | 00$^+$, 5 | 4216.26769 | | | 0.99936 |
| 1 3 0 | $P=5$ | 10$^+$, 3 | 4418.02232 | 4417.95854 | -0.06378 | 0.99886 |
| 0 3 1 | $P=5$ | 10$^-$, 3 | 4426.64338 | 4426.08293 | -0.56045 | 0.99970 |
| 2 1 0 | $P=5$ | 20$^+$, 1 | 4588.84137 | 4589.22600 | 0.38463 | 0.97039 |
| 1 1 1 | $P=5$ | 20$^-$, 1 | 4591.99807 | 4592.18104 | 0.18297 | 0.99970 |
| 0 1 2 | $P=5$ | 11$^+$, 1 | 4643.6204 | 4643.4770 | -0.1434 | 0.97062 |
| 0 6 0 | $P=6$ | 00$^+$, 6 | 5040.84790 | | | 0.99911 |
| 1 4 0 | $P=6$ | 10$^+$, 4 | 5246.10774 | | | 0.99813 |
| 0 4 1 | $P=6$ | 10$^-$, 4 | 5253.16560 | | | 0.99944 |
| 2 2 0 | $P=6$ | 20$^+$, 2 | 5417.41884 | | | 0.97002 |
| 1 2 1 | $P=6$ | 20$^-$, 2 | 5420.5503 | 5421.3007 | 0.7504 | 0.99919 |
| 0 2 2 | $P=6$ | 11$^+$, 2 | 5472.14111 | | | 0.97056 |
| 3 0 0 | $P=6$ | 30$^+$, 0 | 5560.36 | 5560.15 | -0.21 | 0.99146 |
| 2 0 1 | $P=6$ | 30$^-$, 0 | 5560.69 | 5560.74 | 0.05 | 0.99480 |
| 1 0 2 | $P=6$ | 21$^+$, 0 | 5647.40 | 5647.13 | -0.27 | 0.99146 |
| 0 0 3 | $P=6$ | 21$^-$, 0 | 5672.69 | 5672.89 | 0.20 | 0.99500 |
| ν₁ | ν₂ | ν₃ | P   | n₁n₂±, n₄ | E<sub>cal</sub> cm⁻¹ | E<sub>obs</sub> cm⁻¹ | E<sub>obs</sub> - E<sub>cal</sub> cm⁻¹ | %init.ket | (Modulus) |
|---|---|---|---|---|---|---|---|---|---|
| 0  | 7  | 0  | P=7 | 00⁺, 7 | 5859.21285 | | | | |
| 1  | 5  | 0  | | 10⁺, 5 | 6067.85466 | | | | |
| 0  | 5  | 1  | | 10⁻, 5 | 6073.46187 | | | | |
| 2  | 3  | 0  | | 20⁺, 3 | 6239.74543 | | | | |
| 1  | 3  | 1  | | 20⁻, 3 | 6242.85529 | | | | |
| 0  | 3  | 2  | | 11⁺, 3 | 6294.42020 | | | | |
| 3  | 1  | 0  | | 30⁺, 1 | 6384.74 | 6384.63 | -0.11 | | |
| 2  | 1  | 1  | | 30⁻, 1 | 6385.06 | 6384.99 | -0.07 | | |
| 1  | 1  | 2  | | 21⁺, 1 | 6471.82444 | | | | |
| 0  | 1  | 3  | | 21⁻, 1 | 6496.95890 | | | | |
| 0  | 8  | 0  | P=8 | 00⁺, 8 | 6671.36558 | | | | |
| 1  | 6  | 0  | | 10⁺, 6 | 6883.27937 | | | | |
| 0  | 6  | 1  | | 10⁻, 6 | 6887.53650 | | | | |
| 2  | 4  | 0  | | 20⁺, 4 | 7055.82918 | | | | |
| 1  | 4  | 1  | | 20⁻, 4 | 7058.91965 | | | | |
| 0  | 4  | 2  | | 11⁺, 4 | 7110.46700 | | | | |
| 3  | 2  | 0  | | 30⁻, 2 | 7202.89484 | | | | |
| 2  | 2  | 1  | | 30⁻, 2 | 7203.16108 | | | | |
| 1  | 2  | 2  | | 21⁺, 2 | 7293.19251 | | | | |
| 0  | 2  | 3  | | 21⁻, 2 | 7314.97003 | | | | |
| 4  | 0  | 0  | | 40⁺, 0 | 7315.94818 | | | | |
| 3  | 0  | 1  | | 40⁻, 0 | 7315.97536 | | | | |
| 2  | 0  | 2  | | 31⁺, 0 | 7454.90209 | | | | |
| 1  | 0  | 3  | | 31⁻, 0 | 7463.63256 | | | | |
| 0  | 0  | 4  | | 22⁺, 0 | 7519.73558 | | | | |
| 0  | 9  | 0  | P=9 | 00⁺, 9 | 7477.30881 | | | | |
| 1  | 7  | 0  | | 10⁺, 7 | 7692.39210 | | | | |
| 0  | 7  | 1  | | 10⁻, 7 | 7695.39342 | | | | |
| 2  | 5  | 0  | | 20⁺, 5 | 7865.67458 | | | | |
| 1  | 5  | 1  | | 20⁻, 5 | 7868.74925 | | | | |
| 0  | 5  | 2  | | 11⁺, 5 | 7920.28460 | | | | |
| 3  | 3  | 0  | | 30⁺, 3 | 8014.77154 | | | | |
| 2  | 3  | 1  | | 30⁻, 3 | 8014.99941 | | | | |
| 1  | 3  | 2  | | 21⁺, 3 | 8107.35389 | | | | |
Table 3: (cont.)

| $\nu_1$ | $\nu_2$ | $\nu_3$ | Polyad | Local $n_1n_2\pm n_4$ | $E_{\text{cal}}$ cm$^{-1}$ | $E_{\text{obs}}$ cm$^{-1}$ | $E_{\text{obs}}-E_{\text{cal.}}$ cm$^{-1}$ | %init.ket (Modulus) |
|--------|--------|--------|--------|----------------------|---------------------|---------------------|----------------------|----------------------|
| 0      | 3      | 3      | 21$^-$, 3 | 8126.74881           | 0.99357             |
| 4      | 1      | 0      | 40$^+$, 1  | 8129.89865           | 0.99477             |
| 3      | 1      | 1      | 40$^-$, 1  | 8129.92376           | 0.99373             |
| 2      | 1      | 2      | 31$^+$, 1  | 8268.83916           | 0.92604             |
| 1      | 1      | 3      | 31$^-$, 1  | 8277.50278           | 0.99571             |
| 0      | 1      | 4      | 22$^+$, 1  | 8333.53587           | 0.93038             |
| 0      | 10     | 0      | $P=10$ 00$^+$,10 | 8301.04495           | 0.99805             |
| 1      | 8      | 0      | 10$^+$, 8  | 8500.20154           | 0.99430             |
| 0      | 8      | 1      | 10$^-$, 8  | 8506.03621           | 0.99801             |
| 2      | 6      | 0      | 20$^+$, 6  | 8675.26677           | 0.96624             |
| 1      | 6      | 1      | 20$^-$, 6  | 8677.34945           | 0.99523             |
| 0      | 6      | 2      | 11$^+$, 6  | 8726.87621           | 0.96908             |
| 3      | 4      | 0      | 30$^+$, 4  | 8822.39006           | 0.98833             |
| 2      | 4      | 1      | 30$^-$, 4  | 8822.58468           | 0.99028             |
| 1      | 4      | 2      | 21$^+$, 4  | 8910.09790           | 0.98909             |
| 0      | 4      | 3      | 21$^-$, 4  | 8929.29048           | 0.99353             |
| 4      | 2      | 0      | 40$^+$, 2  | 8938.54404           | 0.99280             |
| 3      | 2      | 1      | 40$^-$, 2  | 8938.56874           | 0.99215             |
| 2      | 2      | 2      | 31$^+$, 2  | 9020.00917           | 0.99635             |
| 1      | 2      | 3      | 31$^-$, 2  | 9020.01004           | 0.99636             |
| 0      | 2      | 4      | 22$^+$, 2  | 9077.50764           | 0.92550             |
| 5      | 0      | 0      | 50$^+$, 0  | 9084.10927           | 0.99494             |
| 4      | 0      | 1      | 50$^-$, 0  | 9138.08249           | 0.93036             |
| 3      | 0      | 2      | 41$^+$, 0  | 9212.94838           | 0.97275             |
| 2      | 0      | 3      | 41$^-$, 0  | 9213.22358           | 0.98537             |
| 1      | 0      | 4      | 32$^+$, 0  | 9297.77574           | 0.97546             |
| 0      | 0      | 5      | 32$^-$, 0  | 9335.91658           | 0.98839             |
| 0      | 11     | 0      | $P=11$ 00$^+$,11 | 9070.57613           | 0.99780             |
| 1      | 9      | 0      | 10$^+$, 9  | 9291.71508           | 0.99326             |
| 0      | 9      | 1      | 10$^-$, 9  | 9292.46814           | 0.99761             |
| 2      | 7      | 0      | 20$^+$, 7  | 9466.61462           | 0.96501             |
| 1      | 7      | 1      | 20$^-$, 7  | 9469.72515           | 0.99400             |
| 1      | 7      | 2      | 11$^+$, 7  | 9521.24628           | 0.96859             |
Table 3: (cont.)

| $\nu_1$ | $\nu_2$ | $\nu_3$ | $P$  | $n_1n_2\pm n_4$ | $E_{\text{cal}}$ cm$^{-1}$ | $E_{\text{obs}}$ cm$^{-1}$ | $E_{\text{obs}}-E_{\text{cal.}}$ cm$^{-1}$ | %init.ket (Modulus) |
|---------|---------|---------|------|-----------------|-----------------|-----------------|-------------------------------|------------------|
| 3       | 5       | 0       | 30$^+$, 5 | 9619.75939     |                 |                 |                               | 0.98662          |
| 2       | 5       | 1       | 30$^-$, 5 | 9619.92503     |                 |                 |                               | 0.98828          |
| 1       | 5       | 2       | 21$^+$, 5 | 9716.46600     |                 |                 |                               | 0.98766          |
| 0       | 5       | 3       | 21$^-$, 5 | 9731.60237     |                 |                 |                               | 0.99318          |
| 4       | 3       | 0       | 40$^+$, 3  | 9738.90162     |                 |                 |                               | 0.98995          |
| 3       | 3       | 1       | 40$^-$, 3  | 9738.92598     |                 |                 |                               | 0.98947          |
| 2       | 3       | 2       | 31$^+$, 3  | 9825.56997     |                 |                 |                               | 0.99470          |
| 1       | 3       | 3       | 31$^-$, 3  | 9825.57090     |                 |                 |                               | 0.99480          |
| 0       | 3       | 4       | 22$^+$, 3  | 9877.91234     |                 |                 |                               | 0.92440          |
| 5       | 1       | 0       | 50$^+$, 1  | 9886.46046     |                 |                 |                               | 0.99379          |
| 4       | 1       | 1       | 50$^-$, 1  | 9942.38132     |                 |                 |                               | 0.93010          |
| 3       | 1       | 2       | 41$^+$, 1  | 10017.42136    |                 |                 |                               | 0.97245          |
| 2       | 1       | 3       | 41$^-$, 1  | 10018.67330    |                 |                 |                               | 0.98488          |
| 1       | 1       | 4       | 32$^+$, 1  | 10102.34235    |                 |                 |                               | 0.97509          |
| 0       | 1       | 5       | 32$^-$, 1  | 10139.21647    |                 |                 |                               | 0.98840          |
| 0       | 12      | 0       | $P=12$ 00$^+$,12 | 9857.90423   |                 |                 |                               | 0.99756          |
| 1       | 10      | 0       | 10$^+$,10 | 10081.69213    |                 |                 |                               | 0.99722          |
| 0       | 10      | 1       | 10$^-$,10 | 10081.93920    |                 |                 |                               | 0.99224          |
| 2       | 8       | 0       | 20$^+$, 8  | 10257.73493    |                 |                 |                               | 0.96378          |
| 1       | 8       | 1       | 20$^-$, 8  | 10260.88078    |                 |                 |                               | 0.99275          |
| 0       | 8       | 2       | 11$^+$, 8  | 10312.39973    |                 |                 |                               | 0.96809          |
| 3       | 6       | 0       | 30$^+$, 6  | 10412.83497    |                 |                 |                               | 0.98465          |
| 2       | 6       | 1       | 30$^-$, 6  | 10413.02778    |                 |                 |                               | 0.98612          |
| 1       | 6       | 2       | 21$^+$, 6  | 10511.49437    |                 |                 |                               | 0.98597          |
| 0       | 6       | 3       | 21$^-$, 6  | 10524.68974    |                 |                 |                               | 0.99270          |
| 4       | 4       | 0       | 40$^+$, 4  | 10533.98401    |                 |                 |                               | 0.98648          |
| 3       | 4       | 1       | 40$^-$, 4  | 10534.01023    |                 |                 |                               | 0.98612          |
| Normal \( \nu_1 \) | Polyad \( \nu_2 \) | Local \( \nu_3 \) | \( P \) | \( n_1n_2\pm, n_4 \) | \( E_{\text{cal}} \) | \( E_{\text{obs}} \) | \( E_{\text{obs}} - E_{\text{cal}} \) | \%init.ket (Modulus) |
|---|---|---|---|---|---|---|---|---|
| 2 | 4 | 2 | 31\(^+\), 4 | 10622.75025 | 10622.75101 | 0.99038 |
| 1 | 4 | 3 | 31\(^-\), 4 | 10622.75101 | 10622.75101 | 0.99038 |
| 0 | 4 | 4 | 22\(^+\), 4 | 10673.06131 | 10673.06131 | 0.99214 |
| 5 | 2 | 0 | 50\(^+\), 2 | 10678.75665 | 10678.75667 | 0.99554 |
| 4 | 2 | 1 | 50\(^-\), 2 | 10678.75667 | 10678.75667 | 0.99555 |
| 3 | 2 | 2 | 41\(^+\), 2 | 10681.56493 | 10681.56493 | 0.99235 |
| 2 | 2 | 3 | 41\(^-\), 2 | 10737.44623 | 10737.44623 | 0.99291 |
| 1 | 2 | 4 | 32\(^+\), 2 | 10814.78255 | 10814.78255 | 0.97326 |
| 0 | 2 | 5 | 32\(^-\), 2 | 10815.83798 | 10815.83798 | 0.98356 |
| 6 | 0 | 0 | 60\(^+\), 0 | 10903.29974 | 10903.29974 | 0.97601 |
| 5 | 0 | 1 | 60\(^-\), 0 | 10920.19816 | 10920.19816 | 0.98695 |
| 4 | 0 | 2 | 51\(^+\), 0 | 10920.29123 | 10920.29123 | 0.98798 |
| 3 | 0 | 3 | 51\(^-\), 0 | 10936.26317 | 10936.26317 | 0.98808 |
| 2 | 0 | 4 | 42\(^+\), 0 | 11054.52211 | 11054.52211 | 0.88172 |
| 1 | 0 | 5 | 42\(^-\), 0 | 11070.26392 | 11070.26392 | 0.99042 |
| 0 | 0 | 6 | 33\(^+\), 0 | 11131.78824 | 11131.78824 | 0.89206 |