On the relation between algebraic and configuration space calculations of molecular vibrations

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Abstract

The relation between algebraic and traditional calculations of molecular vibrations is investigated. An explicit connection between interactions in configuration space and the corresponding algebraic interactions is established.

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Ab initio calculations for rovibrational spectra of molecular systems attempt exact solutions of the Schrödinger equation. In practice, the molecular Hamiltonian is usually parametrized as a function of internal coordinates [1] and the potential is modeled in terms of force-field constants, which are determined through calculations involving several configurations associated to the molecular electronic states [2]. For small molecules this procedure is still feasible, but this is in general not the case for polyatomic molecules, due to the large size of the configuration space. It is thus important to develop alternative methods to describe these systems. Algebraic (or vibron) models attempt to provide such alternative techniques [3, 4]. In its original formulation [5, 6] rotations and vibrations were treated simultaneously in terms of coupled $U(4)$ algebras: $\mathcal{G} = U_1(4) \otimes U_2(4) \otimes \ldots$. For polyatomic molecules it was found to be more convenient to first separate the rotations and vibrations and subsequently to treat the vibrations in terms of coupled $U(2)$ algebras: $\mathcal{G} = U_1(2) \otimes U_2(2) \otimes \ldots$. In the latter version of the vibron model the calculation of matrix elements is greatly simplified. An additional advantage is that it is well-suited to incorporate the underlying discrete symmetries [7, 8, 9]. The vibron Hamiltonian, however, is expressed in terms of abstract algebraic operators, whose connection with more traditional methods has been limited to studies of the corresponding energy surface [10].

The aim of this letter is to investigate the relation between algebraic and configuration space calculations and to establish an explicit connection between interaction terms in coordinate space parametrizations and in the more abstract algebraic space. We shall illustrate this connection by studying the Be$_4$ cluster, for which the force field parameters were determined in [11] by ab initio methods. Our comparison is based on an analysis of tetrahedral molecules in terms of symmetry-adapted internal coordinates [12].

In the algebraic approach each relevant interatomic interaction is associated with a $U(2)$ algebra. In the present example of the Be$_4$ cluster, which has a tetrahedral shape, there are six $U(2)$ algebras involved: $\mathcal{G} = U_1(2) \otimes U_2(2) \otimes \ldots \otimes U_6(2)$. Each $U_i(2)$ algebra ($i = 1, \ldots, 6$) is generated by the set $\{\hat{G}_i\} \equiv \{\hat{N}_i,\, \hat{J}_{+,i},\, \hat{J}_{-,i},\, \hat{J}_{0,i}\}$, satisfying the commutation relations

$$[\hat{J}_{0,i}, \hat{J}_{\pm,i}] \;=\; \pm\hat{J}_{\pm,i} \;, \qquad [\hat{J}_{+,i}, \hat{J}_{-,i}] \;=\; 2\hat{J}_{0,i} \;, \qquad [\hat{N}_i, \hat{J}_{\mu,i}] \;=\; 0 \;, \tag{1}$$

with $\mu = \pm, 0$. Here $\hat{N}_i$ is the (boson) number operator and the operators $\hat{J}_{\mu,i}$ satisfy the 'angular momentum' commutation relations of $SU_i(2)$. Since $\vec{\hat{J}}_i^2 = \hat{N}_i(\hat{N}_i + 2)/4$ we can make the identification $j_i = N_i/2$. The eigenvalues of $\hat{J}_{0,i}$ are restricted to $m_i \geq 0$ and can have the values $m_i = N_i/2, (N_i - 2)/2, \ldots, 1/2$ or 0 for N_i odd or even, respectively [4]. The local basis states for each oscillator are usually written as $|N_i, v_i\rangle$, where $v_i = (N_i - 2m_i)/2 = 0, 1, \ldots [N_i/2]$ denotes the number of oscillator quanta in the i-th oscillator. Because of the tetrahedral symmetry of the Be$_4$ cluster $N_i = N$ for the six oscillators. The operators in the model are expressed in terms of the generators of these algebras, and the symmetry requirements of the Hamiltonian under the tetrahedral group $\mathcal{T}_d$ can be readily imposed [9, 13]. In the usual algebraic formulation different chains of subgroups of $\mathcal{G}$ are considered and the Hamiltonian is built by means of appropriate combinations of invariant operators associated to these chains [7, 8, 9]. Here we shall follow a different approach which leads to a richer structure for the Hamiltonian and to a direct connection to configuration space interactions. To achieve this goal we note that the local operators $\{\hat{G}_i\}$ acting on bond i can be projected to any of the $\mathcal{T}_d$ fundamental irreps $\Gamma = A_1$, E and F_2. Using the $\hat{J}_{\mu,i}$

generators of Eq. (1) we obtain the $\mathcal{T}_d$ tensors

$$\hat{T}^{\Gamma}_{\mu,\gamma} \;=\; \sum_{i=1}^{6} \alpha^{\Gamma}_{\gamma,i}\, \hat{J}_{\mu,i} \;, \tag{2}$$

where $\mu = \pm, 0$ and γ denotes the component of Γ. The explicit expressions are given by

$$\begin{aligned}
\hat{T}^{A_1}_{\mu,1} &= \frac{1}{\sqrt{6}} \sum_{i=1}^{6} \hat{J}_{\mu,i} \;, \\
\hat{T}^{E}_{\mu,1} &= \frac{1}{2\sqrt{3}} \left(\hat{J}_{\mu,1} + \hat{J}_{\mu,2} - 2\hat{J}_{\mu,3} + \hat{J}_{\mu,4} - 2\hat{J}_{\mu,5} + \hat{J}_{\mu,6} \right) \;, \\
\hat{T}^{E}_{\mu,2} &= \frac{1}{2} \left(\hat{J}_{\mu,1} - \hat{J}_{\mu,2} - \hat{J}_{\mu,4} + \hat{J}_{\mu,6} \right) \;, \\
\hat{T}^{F_2}_{\mu,1} &= \frac{1}{\sqrt{2}} \left(\hat{J}_{\mu,1} - \hat{J}_{\mu,6} \right) \;, \\
\hat{T}^{F_2}_{\mu,2} &= \frac{1}{\sqrt{2}} \left(\hat{J}_{\mu,2} - \hat{J}_{\mu,4} \right) \;, \\
\hat{T}^{F_2}_{\mu,3} &= \frac{1}{\sqrt{2}} \left(\hat{J}_{\mu,3} - \hat{J}_{\mu,5} \right) \;.
\end{aligned} \tag{3}$$

The algebraic Hamiltonian can now be constructed by repeated couplings of these tensors to a total symmetry A_1, since it must commute with all operations in $\mathcal{T}_d$. This is accomplished by means of the $\mathcal{T}_d$ Clebsch-Gordan coefficients [9, 13].

In order to establish a connection with configuration space calculations we use the analysis of [12]. In this work the vibrational Hamiltonian for the Be$_4$ cluster is expressed in terms of symmetry-adapted internal coordinates, q^{Γ}_{γ}, and momenta, p^{Γ}_{γ}. The transformation to the tensor operators of Eqs. (2,3) proceeds in two steps. First we introduce creation and annihilation operators

$$b^{\Gamma\,\dagger}_{\gamma} \;=\; \frac{1}{\sqrt{2}} \left(q^{\Gamma}_{\gamma} - i p^{\Gamma}_{\gamma} \right) \;, \qquad b^{\Gamma}_{\gamma} \;=\; \frac{1}{\sqrt{2}} \left(q^{\Gamma}_{\gamma} + i p^{\Gamma}_{\gamma} \right) \;. \tag{4}$$

Here the normal boson operators are related to the local boson operators by $b^{\Gamma}_{\gamma} = \sum_i \alpha^{\Gamma}_{\gamma,i}\, b_i$. The coefficients $\alpha^{\Gamma}_{\gamma\, i}$ can be read from Eqs. (2,3). Next the local boson operators are associated with the generators of Eq. (1) by means of

$$b_i \rightarrow \hat{J}_{+,i}/\sqrt{N_i} \;, \qquad b^{\dagger}_i \rightarrow \hat{J}_{-,i}/\sqrt{N_i} \;. \tag{5}$$

This transformation is such that the commutator

$$\frac{1}{N_i}[\hat{J}_{+,i}, \hat{J}_{-,i}] \;=\; \frac{1}{N_i} 2\hat{J}_{0,i} \;=\; \frac{1}{N_i}(\hat{N}_i - 2\hat{v}_i) \;=\; 1 - \frac{2\hat{v}_i}{N_i} \;, \tag{6}$$

reduces for $N_i \rightarrow \infty$ to the standard boson commutator $[b_i, b^{\dagger}_i] = 1$. Eq. (5) provides a procedure to construct an anharmonic representation of harmonic operators. The anharmonic contribution arises from the $-2\hat{v}_i/N_i$ term in Eq. (6). Note that each local harmonic oscillator $(b^{\dagger}_i b_i + b_i b^{\dagger}_i)/2$ leads to $(\hat{J}_{-,i}\hat{J}_{+,i} + \hat{J}_{+,i}\hat{J}_{-,i})/2N_i = \hat{v}_i + 1/2 - \hat{v}^2_i/N_i$ and thus to a Morse-like spectrum through the association of Eq. (5). In this way the algebraic model substitutes harmonic oscillators by anharmonic ones.

This procedure can be applied to the various contributions to the vibrational Hamiltonian for the Be$_4$ cluster [12]. The vibrational basis states for this system are usually labeled by $(\nu_1, \nu_2^m, \nu_3^l)$ [14]. Here ν_1,

ν_2 and ν_3 denote the number of phonons in the A_1, E and F_2 modes, respectively, and $m = \nu_2, \nu_2 - 2, \ldots, 1$ (or 0) for ν_2 odd (or even) and and $l = \nu_3, \nu_3 - 2, \ldots, 1$ (or 0) for ν_3 odd (or even) are the vibrational angular momenta associated with the E and F_2 modes. For the zeroth order vibrational Hamiltonian we find

$$H_0 \;=\; \omega_1 \, \hat{\mathcal{H}}_{A_1} + \omega_2 \, \hat{\mathcal{H}}_E + \omega_3 \, \hat{\mathcal{H}}_{F_2} \;, \tag{7}$$

with

$$\hat{\mathcal{H}}_\Gamma \;=\; \frac{1}{2N} \sum_\gamma \left(\hat{T}^\Gamma_{-,\gamma} \hat{T}^\Gamma_{+,\gamma} + \hat{T}^\Gamma_{+,\gamma} \hat{T}^\Gamma_{-,\gamma} \right) \;. \tag{8}$$

The anharmonic vibrational terms are expressed in terms of products of $\hat{\mathcal{H}}_\Gamma$,

$$\begin{aligned} H_1 \;=\; & X_{11} \left(\hat{\mathcal{H}}_{A_1} \right)^2 + X_{22} \left(\hat{\mathcal{H}}_E \right)^2 + X_{33} \left(\hat{\mathcal{H}}_{F_2} \right)^2 \\ & + X_{12} \left(\hat{\mathcal{H}}_{A_1} \hat{\mathcal{H}}_E \right) + X_{13} \left(\hat{\mathcal{H}}_{A_1} \hat{\mathcal{H}}_{F_2} \right) + X_{23} \left(\hat{\mathcal{H}}_E \hat{\mathcal{H}}_{F_2} \right) \;. \end{aligned} \tag{9}$$

The further splitting of vibrational levels (ν_1, ν_2, ν_3) into its possible sublevels is achieved by means of the interactions [12]

$$\begin{aligned} H_2 \;=\; & g_{22} \left(\hat{l}^{A_2} \right)^2 + g_{33} \sum_\gamma \hat{l}^{F_1}_\gamma \, \hat{l}^{F_1}_\gamma \\ & + t_{33} \left(6 \sum_\gamma [\hat{T}^{F_2}_- \times \hat{T}^{F_2}_-]^E_\gamma \, [\hat{T}^{F_2}_+ \times \hat{T}^{F_2}_+]^E_\gamma - 4 \sum_\gamma [\hat{T}^{F_2}_- \times \hat{T}^{F_2}_-]^{F_2}_\gamma \, [\hat{T}^{F_2}_+ \times \hat{T}^{F_2}_+]^{F_2}_\gamma \right) \frac{1}{N^2} \\ & + t_{23} \left(8 \sum_\gamma [\hat{T}^E_- \times \hat{T}^{F_2}_-]^{F_1}_\gamma \, [\hat{T}^E_+ \times \hat{T}^{F_2}_+]^{F_1}_\gamma - 8 \sum_\gamma [\hat{T}^E_- \times \hat{T}^{F_2}_-]^{F_2}_\gamma \, [\hat{T}^E_+ \times \hat{T}^{F_2}_+]^{F_2}_\gamma \right) \frac{1}{N^2} \;. \end{aligned} \tag{10}$$

The operators $\hat{l}^{A_2}$ and $\hat{l}^{F_1}$ represent the vibrational angular momentum operators associated with the E and F_2 modes, respectively,

$$\begin{aligned} \hat{l}^{A_2} \;&=\; -i \, \sqrt{2} \frac{1}{N} [\hat{T}^E_- \times \hat{T}^E_+]^{A_2} \;, \\ \hat{l}^{F_1}_\gamma \;&=\; +i \, \sqrt{2} \frac{1}{N} [\hat{T}^{F_2}_- \times \hat{T}^{F_2}_+]^{F_1}_\gamma \;. \end{aligned} \tag{11}$$

The square brackets in Eqs. (10,11) denote the tensor coupling under the point group $\mathcal{T}_d$

$$[\hat{T}^{\Gamma_1} \times \hat{T}^{\Gamma_2}]^\Gamma_\gamma \;=\; \sum_{\gamma_1, \gamma_2} C(\Gamma_1, \Gamma_2, \Gamma; \gamma_1, \gamma_2, \gamma) \, \hat{T}^{\Gamma_1}_{\gamma_1} \, \hat{T}^{\Gamma_2}_{\gamma_2} \;, \tag{12}$$

where the expansion coefficients are the Clebsch-Gordan coefficients for $\mathcal{T}_d$ [9, 13]. The interactions of Eq. (10) were absent in previous versions of the model [5, 6, 7].

The algebraic Hamiltonian of Eqs (7–12) is the algebraic equivalent of the vibrational Hamiltonian of [12]. The harmonic frequencies ω_i and anharmonic constants X_{ij}, g_{22}, g_{33}, t_{33} and t_{23} have the same meaning as in [12] and the ab initio calculations of [11] can be used to generate the spectrum. The various contributions to the algebraic Hamiltonian arise naturally from the successive couplings of the fundamental tensors of Eq. (3). The scale transformation of Eq. (5) makes it possible to establish the connection between ab initio and algebraic parameteres and to explicitly construct the algebraic interactions that correspond to interactions in configuration space. In the opposite sense, Eqs. (5,6) provide a procedure to obtain a geometric interpretation of algebraic interactions in terms of those in configuration space. In the harmonic limit, which is defined as $N_i \to \infty$, Eq. (6) reduces to the standard boson commutator $[b_i, b_i^\dagger] = 1$. This limit corresponds to a contraction of $SU_i(2)$ to the Weyl algebra, generated by the set $\{b_i, b_i^\dagger, 1\}$. In the harmonic limit the Hamiltonian $H_0 + H_1 + H_2$ of Eqs. (7–12) reduces *exactly* to the vibrational Hamiltonian of [12]. Note that because of the replacement of Eq. (5) the Hamiltonian $H_0 + H_1 + H_2$ only depends on the $\hat{T}^{\Gamma}_{\mu,\gamma}$ tensors of Eq. (3) with $\mu = \pm$. In addition, the algebraic model provides terms involving the $\hat{T}^{\Gamma}_{\mu,\gamma}$ tensors with $\mu = 0$. As can be seen from Eq. (6) these terms are completely anharmonic in origin and have no direct counterpart in models based on the standard harmonic bosons. These operators arise from the substitution of harmonic oscillators by Morse oscillators and play an important role when dealing with anharmonic molecules, particularly at higher phonon numbers [15].

Apart from providing a direct connection to configuration space calculations, this formalism can also be used as an effective model of molecular vibrations, particularly when no ab initio calculations are available. As an example, we show in Table I the results of a fit to the ab initio calculations for Be$_4$ up to four phonons. The ab initio results were generated with the parameters from [11]. The Hamiltonian used in the fit contains 9 interaction terms compared to the 13 of [12] (see Eqs. (7,9,10)). The parameters are extracted in a fit that includes all vibrational energies up to four phonons ($V = \nu_1 + \nu_2 + \nu_3 \leq 4$): $\omega_1 = 636$, $\omega_2 = 453$, $\omega_3 = 532$, $X_{33} = 44.276$, $X_{12} = 4.546$, $X_{13} = -2.539$, $g_{33} = -15.031$, $t_{33} = -1.679$ and $t_{23} = -1.175$. All values are given in cm^{-1}. The total number of bosons used in the fit is $N = 44$. The r.m.s. deviation between the algebraic and the ab initio calculations is 2.6 cm^{-1}.

As a test of the predictive power of the algebraic approach we have performed another calculation in which the same 9 parameters were determined in a fit that only included the vibrational energies up to three phonons ($V \leq 3$). In this case the r.m.s. deviation is 1.6 cm^{-1}. If we now use these values of the parameters to calculate the four phonon states, the r.m.s. increases to only 3.1 cm^{-1}, compared to 2.6 cm^{-1} in the previous calculation. We remark that by restricting the model interactions to Casimir invariants and their powers [5, 6, 7] the Be$_4$ spectrum cannot be reproduced. The terms in H_2 of Eq. (10) play a crucial role.

Repeating the same fit in the harmonic limit ($N \to \infty$) the r.m.s. deviation increases from 2.6 to 5.4 cm^{-1}. This shows that the anharmonic contributions introduced by taking a finite value of N (see Eq. (6)) provide an important improvement of the fit. The real test of this aspect is a fit to experimental data rather than to other calculations. Work on the application of this algebraic model to the experimental vibrational spectra of polyatomic molecules is in progress [15].

In summary, in this letter we have established a connection between algebraic and configuration-space interactions. For the example of the Be$_4$ cluster (with tetrahedral symmetry) we have, starting from configuration space interactions, constructed explicitly the corresponding algebraic interactions (which have a richer structure than in previous versions of the model). In the harmonic limit the configuration space results are reproduced exactly.

In addition, it was shown that the algebraic model can also be used as an effective model of molecular vibrations with good precision. In the algebraic approach the eigenvalues and corresponding wave functions are obtained by matrix diagonalization. Hence the required computing time is small. These properties open the possibility to use the algebraic model as a numerically efficient, empirical tool to study molecular vibrations, especially when no ab initio calculations are available (or feasible) [15].

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Table I: Vibrational excitations of Be_4 using the algebraic Hamiltonian with parameters given in the text. The ab initio ($N \rightarrow \infty$) spectrum is generated with the parameters from [11]. The energies are given in cm^{-1}.

V	$(\nu_1, \nu_2^m, \nu_3^l)$	Γ	Ab initio $N \rightarrow \infty$	Fit $N = 44$	V	$(\nu_1, \nu_2^m, \nu_3^l)$	Γ	Ab initio $N \rightarrow \infty$	Fit $N = 44$
1	$(1, 0^0, 0^0)$	A_1	638.6	637.0	3	$(1, 0^0, 2^0)$	A_1	2106.8	2105.6
	$(0, 1^1, 0^0)$	E	453.6	455.0		$(1, 0^0, 2^2)$	E	2000.1	1999.8
	$(0, 0^0, 1^1)$	F_2	681.9	678.2			F_2	2056.8	2052.8
2	$(2, 0^0, 0^0)$	A_1	1271.0	1269.2		$(0, 3^1, 0^0)$	E	1341.3	1343.7
	$(1, 1^1, 0^0)$	E	1087.1	1087.0		$(0, 3^3, 0^0)$	A_1	1355.5	1352.5
	$(1, 0^0, 1^1)$	F_2	1312.6	1308.3			A_2	1355.5	1354.4
	$(0, 2^0, 0^0)$	A_1	898.3	901.4		$(0, 2^{0,2}, 1^1)$	F_2	1565.5	1565.7
	$(0, 2^2, 0^0)$	E	905.4	906.1			F_2	1584.4	1583.1
	$(0, 1^1, 1^1)$	F_1	1126.7	1125.1		$(0, 2^2, 1^1)$	F_1	1578.5	1578.0
		F_2	1135.5	1134.1		$(0, 1^1, 2^{0,2})$	E	1821.4	1821.6
	$(0, 0^0, 2^0)$	A_1	1484.0	1483.0			E	1929.5	1929.0
	$(0, 0^0, 2^2)$	E	1377.3	1373.9		$(0, 1^1, 2^2)$	A_2	1813.3	1813.1
		F_2	1434.1	1429.6			A_1	1830.8	1831.7
3	$(3, 0^0, 0^0)$	A_1	1897.0	1896.7			F_2	1874.4	1873.2
	$(2, 1^1, 0^0)$	E	1714.3	1714.3			F_1	1883.2	1883.0
	$(2, 0^0, 1^1)$	F_2	1937.0	1933.7		$(0, 0^0, 3^{1,3})$	F_2	2136.5	2134.2
	$(1, 2^0, 0^0)$	A_1	1526.6	1529.2			F_2	2327.3	2326.9
	$(1, 2^2, 0^0)$	E	1533.7	1532.8		$(0, 0^0, 3^3)$	F_1	2199.8	2197.1
	$(1, 1^1, 1^1)$	F_1	1752.2	1749.7			A_1	2256.5	2254.4
		F_2	1761.0	1759.8					

Table I: Continued.

V	$(\nu_1, \nu_2^m, \nu_3^l)$	Γ	Ab initio	Fit	V	$(\nu_1, \nu_2^m, \nu_3^l)$	Γ	Ab initio	Fit
			$N \to \infty$	$N = 44$				$N \to \infty$	$N = 44$
4	$(4, 0^0, 0^0)$	A_1	2516.8	2519.5	4	$(0, 4^4, 0^0)$	E	1803.8	1797.1
	$(3, 1^1, 0^0)$	E	2335.2	2336.9		$(0, 3^{1,3}, 1^1)$	F_1	1998.9	2000.1
	$(3, 0^0, 1^1)$	F_2	2555.1	2554.4			F_2	2013.3	2014.0
	$(2, 2^0, 0^0)$	A_1	2148.7	2152.2			F_1	2026.4	2025.0
	$(2, 2^2, 0^0)$	E	2155.8	2154.8			F_2	2029.5	2024.7
	$(2, 1^1, 1^1)$	F_1	2371.5	2369.8		$(0, 2^{0,2}, 2^{0,2})$	E	2247.8	2251.0
		F_2	2380.2	2380.7			A_1	2262.1	2263.0
	$(2, 0^0, 2^0)$	A_1	2723.2	2723.6			E	2273.9	2276.6
	$(2, 0^0, 2^2)$	E	2616.5	2620.8			A_1	2367.6	2367.0
		F_2	2673.3	2671.4			E	2373.1	2371.1
	$(1, 3^1, 0^0)$	E	1964.4	1967.1		$(0, 2^{0,2}, 2^2)$	F_2	2308.8	2310.9
	$(1, 3^3, 0^0)$	A_1	1978.7	1973.6			F_2	2327.7	2330.2
		A_2	1978.7	1975.2		$(0, 2^2, 2^2)$	A_2	2265.1	2268.2
	$(1, 2^{0,2}, 1^1)$	F_2	2185.8	2185.3			F_1	2321.8	2321.9
		F_2	2204.8	2204.5		$(0, 1^1, 3^{1,3})$	F_1	2567.1	2570.0
	$(1, 2^2, 1^1)$	F_1	2198.9	2197.7			F_2	2585.5	2588.3
	$(1, 1^1, 2^{0,2})$	E	2438.9	2443.5			F_1	2639.9	2643.1
		E	2547.1	2545.7			F_2	2640.1	2643.0
	$(1, 1^1, 2^2)$	A_2	2430.9	2431.8			F_1	2764.3	2764.9
		A_1	2448.4	2455.1			F_2	2772.0	2779.7
		F_2	2492.0	2491.0		$(0, 1^1, 3^3)$	E	2696.8	2700.3
		F_1	2500.8	2501.5		$(0, 0^0, 4^{0,4})$	A_1	2909.1	2906.1
	$(1, 0^0, 3^{1,3})$	F_2	2751.2	2748.4			A_1	3290.9	3290.5
		F_2	2942.1	2942.6		$(0, 0^0, 4^{2,4})$	E	2956.1	2952.6
	$(1, 0^0, 3^3)$	F_1	2814.5	2816.6			F_2	3067.3	3067.3
		A_1	2871.3	2870.7			E	3137.2	3134.9
	$(0, 4^0, 0^0)$	A_1	1775.3	1776.8			F_2	3253.0	3253.7
	$(0, 4^2, 0^0)$	E	1782.5	1781.6		$(0, 0^0, 4^4)$	F_1	2978.9	2978.0