DETERMINATION OF THE NUCLEAR SPIN STATISTICAL WEIGHTS FOR THE ROTATION-INTERNAL ROTATION-INVERSION LEVELS OF METHYLAMINE

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Abstract

A complete derivation of the nuclear statistical weights for the rotation-internal rotation-inversion levels of methylamine is given using the permutation-inversion transformation properties of the nuclear spin wavefunctions and the rotation-internal rotation-inversion eigenfunctions.

Introduction

From the theory of vibrotors it is well known that the absorption coefficient of a rotation-vibration transition is proportional to the nuclear spin statistical weight of the levels between which the transition takes place. To determine the nuclear spin statistical weights for levels of flexible molecules having hindered large amplitude internal motions is generally impossible with the method used for rigid molecules.

The aim of the present paper is to derive the nuclear spin statistical weights for levels of methylamine. These data have been determined by Kręglewski [1] exploiting the analogy with methyl boron difluoride [2], however, no complete derivation has been given. The derivation described in the present paper is general, it can be used for all flexible molecules. The method is based on the symmetry properties of the eigenfunctions. In contrast to rigid molecules where point groups and the rotational group can be used to describe the symmetry properties of eigensystems, for flexible molecules,—like methylamine which has two different types of hindered large amplitude internal motions (see e.g. [3])—, the permutation-inversion (PI) group theory has to be applied.

The permutation-inversion (PI) group of methylamine

The permutation-inversion (PI) group theory was elaborated by Longuet–Higgins [2] and Hougen [4, 5] for classifying the eigensystems of flexible molecules which tunnel among different configurations varying continuously the point group symmetry. This theory is a very efficient tool in the molecular spectroscopy of flexible molecules. Beside the symmetry classification of molecular eigensystems it can be successfully used to obtain selection rules for transitions, to simplify considerably the theory of molecular motions, to increase the speed of numerical calculations and last but not least to derive nuclear spin statistical weights of energy levels.

The permutation-inversion group as all molecular symmetry groups is formed by a set of operations which leaves the molecular Hamiltonian unchanged. The PI group elements are [2]:

    i. the identity E,

    ii. the permutation P of positions and spins of identical nuclei or the products of such permutations,

    iii. the permutation-inversion $P = PE^* = E^*P$ where E^* is the inversion of the positions of all particles in the center of mass.

The number of elements of a complete PI group is given by

$$2 \prod_{k=1}^{m} n_k!$$

where n_k denotes the number of nuclei in the k-th identical atom set [6]. E.g. the methylamine molecule contains two atom sets with two and three identical atoms, respectively. Thus there are 24 elements in the complete PI group of methylamine:

$$E; \quad (567), (576); \quad (67)^*, (57)^*, (56)^*; \quad (12);$$

$$(12)(567), (12)(576); \quad (12)(67)^*, (12)(57)^*, (12)(56)^*; \tag{1a}$$

$$E^*; \quad (567)^*, (576)^*; \quad (67), (57), (56); \quad (12)^*;$$

$$(12)(567)^*, (12)(576)^*; \quad (12)(67), (12)(57), (12)(56); \tag{1b}$$

where the numbers in the brackets denote the permuted atoms. For example the permutation (567) is a cyclic permutation of the hydrogen nuclei in the methyl group, which is equivalent to the product of two simple permutations, i.e. $(567) = (67)(56)$. The numbering of nuclei is shown in Fig. 1, the effects of operations upon the molecule are depicted in Fig. 2a, b.

For the symmetry problems of flexible molecules it is not the complete PI group but the so called PI group (a subgroup of the complete PI one) that has to be applied. The complete PI group consists of feasible and infeasible
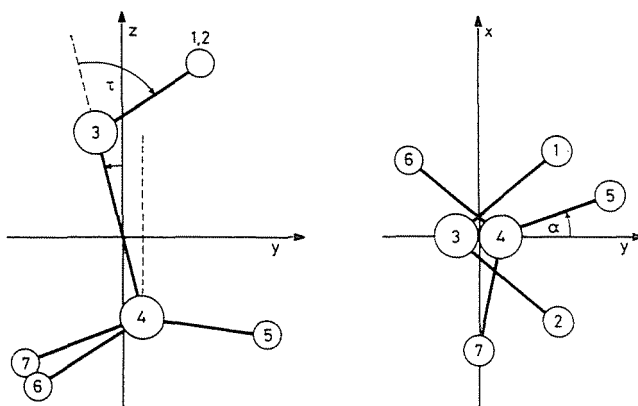
Fig. 1. Numbering of the atoms of methylamine. The angles α and τ denote the coordinates of internal rotation and inversion, respectively

operations. According to Longuet–Higgins' concept an operation is feasible if it can be achieved during the time of the experiment [2]. The PI group of a molecule is obtained by deleting all infeasible elements from the complete PI one.

In order to clarify the deeper meaning of feasibility, we consider each operation as sum of an "equivalent rotation" and hindered large amplitude motions (see for methylamine in Ref. [3]). An "equivalent rotation" describes the effect of a PI element on the Euler angles. Since the "equivalent rotations" are always unhindered, a PI operation consisting of only an "equivalent rotation" is feasible. Thus the feasibility of an operation is determined by the barrier heights of the large amplitude motions. E.g. if one of the barriers is low, all elements requiring the tunnelling of only this low barrier are feasible. There is, of course, no absolute criterion for the feasibility of a given element. For instance if the energy of an excited level is comparable to the barrier, the probability of penetrating and therefore the associated speed of the tunnelling the barrier will be greater than for lower energy levels. Elements that are not feasible for lower energies can be therefore feasible for higher energies. From this it may be seen that the PI group theory is a very flexible and efficient one.

Comparing the elements of the complete PI group of methylamine it can be shown that all elements in Fig. 2a are feasible, and all the ones in Fig. 2b are infeasible. The operations in Fig. 2a require the tunnelling of only the barriers of internal rotation and inversion beside the "equivalent rotations" (see Table I). The probabilities of penetrating these barriers are relatively high. The operations in Fig. 2b require also interchanges of protons (see Table II), e.g. the element E^* consists of an "equivalent rotation" C_2^y and the change of proton 6 for 7. The speed of these interchanges is practically zero.
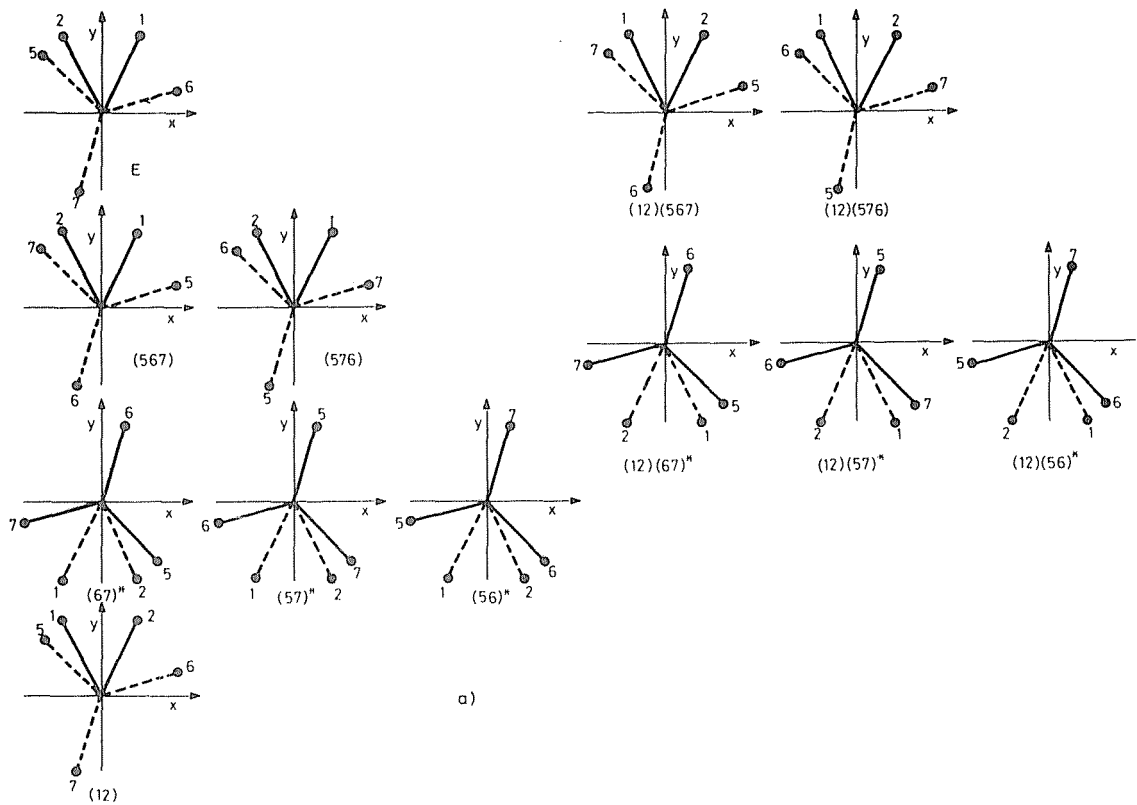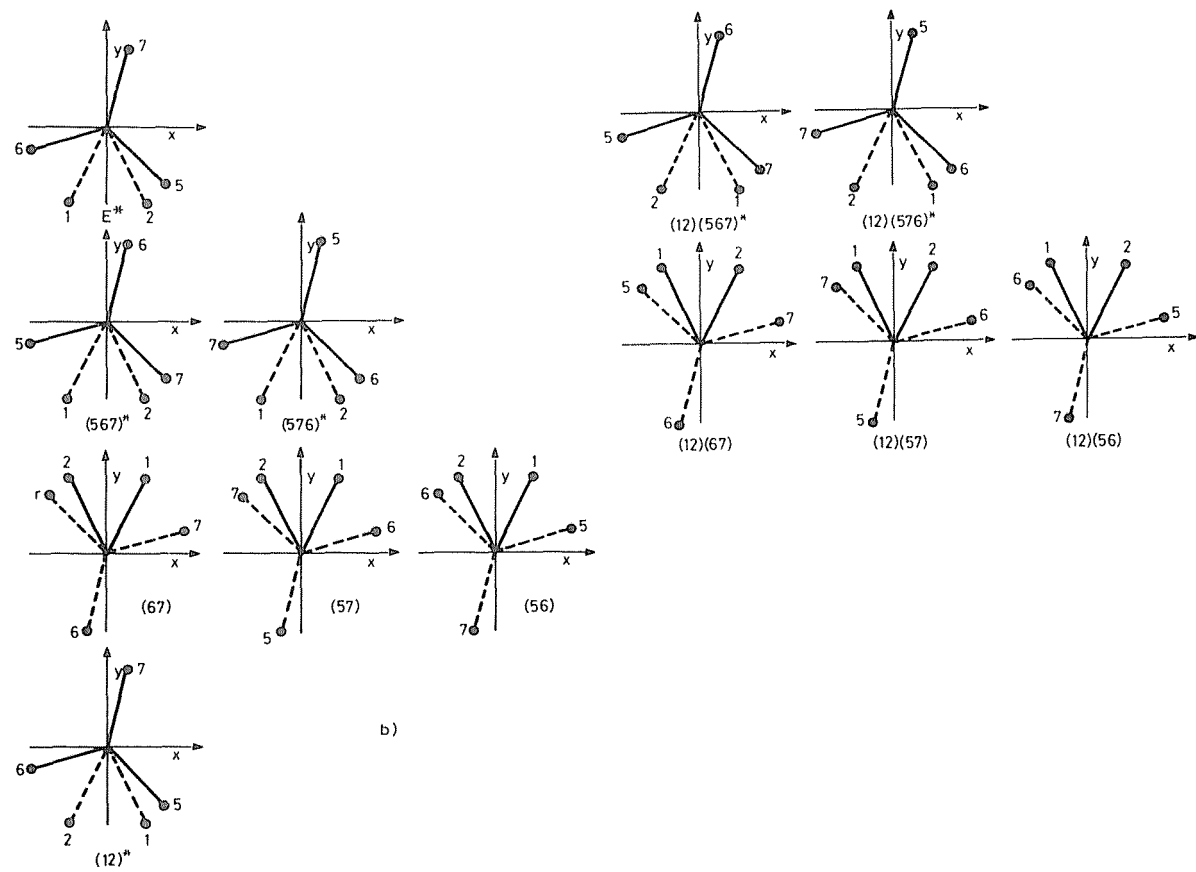
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Fig. 2. a) The effects of the feasible elements of the complete PI group upon methylamine

b) The effects of the infeasible elements of the complete PI group upon methylamine

Table I

The feasible elements of the complete PI group of methylamine[a]

	E	(567) (576)	(56)* (67)* (57)*	(12)	(12)(567) (12)(576)	(12)(56)* (12)(67)* (12)(57)*
Eq. rot.	E	E	C_2^y	C_2^x	C_2^z	C_2^x
$iR_a^{z'}$	$\alpha\to\alpha$	$\alpha\to\alpha-\dfrac{2\pi}{3}$ $\alpha\to\alpha+\dfrac{2\pi}{3}$	$\alpha\to-\alpha-\dfrac{\pi}{3}$ $\alpha\to-\alpha-\pi$ $\alpha\to-\alpha+\dfrac{\pi}{3}$	$\alpha\to\alpha+\pi$	$\alpha\to\alpha+\dfrac{\pi}{3}$ $\alpha\to\alpha-\dfrac{\pi}{3}$	$\alpha\to-\alpha+\dfrac{2\pi}{3}$ $\alpha\to-\alpha$ $\alpha\to-\alpha-\dfrac{2\pi}{3}$
$I_\tau^{\tau'}$	$\tau\to\tau$	$\tau\to\tau$	$\tau\to-\tau$	$\tau\to-\tau$	$\tau\to-\tau$	$\tau\to\tau$

[a] Superscript α' in the operator iR and superscript τ' in the operator I indicate the new values of the coordinates after tunnelling the barriers [3].

Table II

The infeasible elements of the complete PI group of methylamine[b]

	E*	(567)* (576)*	(56) (67) (57)	(12)*	(12)(567)* (12)(576)*	(12)(56) (12)(67) (12)(57)
Eq. rot.	C_2^y	C_2^x	E	C_2^x	C_2^z	C_2^z
$iR_a^{z'}$	$\alpha\to\alpha+\dfrac{\pi}{2}$	$\alpha\to-\alpha-\dfrac{\pi}{3}$ $\alpha\to-\alpha+\dfrac{\pi}{3}$	$\alpha\to\alpha$	$\alpha\to\alpha+\pi$	$\alpha\to-\alpha-\dfrac{\pi}{3}$ $\alpha\to-\alpha+\dfrac{\pi}{3}$	$\alpha\to\alpha+\pi$
$I_\tau^{\tau'}$	$\tau\to-\tau$	$\tau\to-\tau$	$\tau\to\tau$	$\tau\to\tau$	$\tau\to\tau$	$\tau\to-\tau$
Interchange of protons	$6\leftrightarrow7$	$6\leftrightarrow7$	$6\leftrightarrow7$ $5\leftrightarrow7$ $5\leftrightarrow6$	$6\leftrightarrow7$	$6\leftrightarrow7$	$6\leftrightarrow7$ $5\leftrightarrow7$ $5\leftrightarrow6$

[b] Each operation contains only one interchange of protons.

It is necessary to note that in Bunker's terminology the term "complete nuclear PI group" (CNPI) is used for the complete PI group whereas PI is called molecular symmetry group [7].

The derivation of the nuclear spin statistical weights

The nuclear spin statistical weight of a rotation-internal rotation-inversion level of methylamine,—like the rotation levels of nonflexible molecules—, is defined by the number of the different nuclear spin quantum states corresponding to the given level. These spin states take their origin from the presence of atomic nuclei with nonzero spin momenta and correspond to the different projections of the spins along a chosen direction. In the absence of external fields the energy of all projections is the same. However, for a given level different spin states can be realized depending on its symmetry, i.e. the levels have in general different nuclear spin statistical weights. The number of allowed states can be derived by group theoretical considerations.

The total wavefunction of methylamine can be written as a product of the electron, the vibration, the rotation-internal rotation-inversion, the nuclear spin and the electron spin eigenfunctions:

$$\Psi_t = \Psi_e \Psi_v \Psi_{riri} \Psi_{ns} \Psi_{es} . \tag{2}$$

It is assumed here that all electrons and all vibrations of the molecule are in ground state, i.e. Ψ_e, Ψ_v and Ψ_{es} are totally symmetric. The forms and the symmetry properties of eigenfunctions Ψ_{riri} of methylamine have been given in our previous paper [3].

According to the generalized Pauli Exclusion Principle Ψ_t is changed in sign by any permutation P that involves odd number permutations of nuclei having half integer spin (fermions):

$$P\Psi_t = -\Psi_t . \tag{3}$$

However, if the inversion operation E^* is applied to Ψ_t the sign can be either $+$ or $-$, i.e.:

$$E^*\Psi_t = \pm \Psi_t . \tag{4}$$

From the results it can be seen that the total wavefunction Ψ_t has to belong to such species in which the characters of operations P involving odd number permutations of fermions are always -1. In the case of methylamine these species are A_1'' and A_2'', respectively (see Table III). Here the allowed species doubles according to the double-valued eigenstate of operation E^*. It is necessary to note that in the theory of PI groups the species are labelled by the irreducible representations of the point group isomorphic with the given PI group. Thus in the case of methylamine this is the point group D_{3h}.

Since the product $\Psi_e \Psi_v \Psi_{es}$ in ground state belongs to the total symmetric species A_1', instead of Ψ_t it is enough to disscuss only the symmetry of the product $\Psi_{riri} \Psi_{ns}$. The representations of this product can be derived as direct

Table III

Character table of the permutation-inversion group of methylamine isomorphic with the point group D_{3h}

Species	E	(567) (576)	(56)* (67)* (57)*	(12)	(12)(567) (12)(576)	(12)(56)* (12)(67)* (12)(57)*
A'_1	1	1	1	1	1	1
A'_2	1	1	-1	1	1	-1
A''_1	1	1	1	-1	-1	-1
A''_2	1	1	-1	-1	-1	1
E'	2	-1	0	2	-1	0
E''	2	-1	0	-2	1	0

products from the species of the two constituents. It is obvious that for a given level only such nuclear spin states are allowed for which it holds [7]:

$$\Gamma(\Psi_{riri}) \otimes \Gamma(\Psi_{ns})^{tot} \supset \Gamma(\Psi_t) = (A''_1, A''_2), \tag{5}$$

where $\Gamma(\Psi_t)$ denotes the species to which Ψ_t has to belong, i.e. A''_1 and A''_2. $\Gamma(\Psi_{riri})$ is the species of the given rotation-internal rotation-inversion level and $\Gamma(\Psi_{ns})^{tot}$ denotes the full representation of the nuclear spin functions. The number of species A''_1 and A''_2 in the direct product is the nuclear spin statistical weight.

In the following the nuclear spin eigenfunctions will be built up. All nuclear spin functions can be written as a product of the functions of identical atom sets, i.e. in our case:

$$\Psi_{ns} = \Psi_{ns}^{(12)} \Psi_{ns}^{(567)}. \tag{6}$$

From this follows that:

$$\Gamma(\Psi_{ns}) = \Gamma(\Psi_{ns}^{(12)}) \otimes \Gamma(\Psi_{ns}^{(567)}). \tag{7}$$

The nuclear spin functions of identical atom sets can be represented by the usual products of atomic spin functions $\alpha_{(k)}$ and $\beta_{(k)}$ where $\alpha_{(k)}$ is the symmetric spin function of the k-th hydrogen atom and $\beta_{(k)}$ is the antisymmetric one.

If $\hat{S}$ denotes the operator of the atomic spin angular momentum and $\hat{S}_z$ denotes the z component of $\hat{S}$, the eigenvalues for a single proton in $\hbar$ units are:

$$\hat{S}_z \alpha_{(k)} = \frac{1}{2} \alpha_{(k)}, \tag{8a}$$

or

$$\hat{S}_z \beta_{(k)} = -\frac{1}{2} \beta_{(k)}, \tag{8b}$$

and

$$\hat{S}^2\alpha_{(k)} = I_{ns}(I_{ns}+1)\alpha_{(k)}, \qquad (8c)$$

or

$$\hat{S}^2\beta_{(k)} = I_{ns}(I_{ns}+1)\beta_{(k)}, \qquad (8d)$$

where the quantum number I_{ns} of the atomic spin angular momentum is $1/2$. Both the values $1/2$ and $-1/2$ in Eq. (8a, b) are the quantum numbers m_{ns} of $\hat{S}_z$.

If an identical atom set contains m protons the total number of nuclear spin states in this set is given by the expression $(2I_{ns}+1)^m$. The nuclear spin functions of the two atom sets of methylamine and their resultant quantum numbers m_s are collected in Table IV. Table V gives the characters of the reducible (or irreducible) representations to which these functions belong. The full representations of the two sets obtained as a direct sum of the derived representations are given also in Table V. In the transformation of the products $\alpha\beta$ it has been taken into account that:

    i. Only the operations P act on the functions which are invariant under E^*, so the nuclear spin wavefunctions are transformed by P^* and P in the same way.

Table IV

The nuclear spin functions $\Psi_{n3}^{(12)}$ of the group NH_2

		Resultant quantum number of the group
1.	$\alpha(1)\alpha(2)$	$m_s = +1$
2.	$\alpha(1)\beta(2), \ \beta(1)\alpha(2)$	$m_s = \ \ 0$
3.	$\beta(1)\beta(2)$	$m_s = -1$

The nuclear spin functions $\Psi_{ns}^{(567)}$ of the group CH_3

		Resultant quantum number of the group
1	$\alpha(5)\alpha(6)\alpha(7)$	$m_s = +1\frac{1}{2}$
2. 3. 4.	$\alpha(5)\alpha(6)\beta(7)$ $\alpha(5)\beta(6)\alpha(7)$ $\beta(5)\alpha(6)\alpha(7)$	$m_s = +\frac{1}{2}$
5. 6. 7.	$\beta(5)\beta(6)\alpha(7)$ $\beta(5)\alpha(6)\beta(7)$ $\alpha(5)\beta(6)\beta(7)$	$m_s = -\frac{1}{2}$
8.	$\beta(5)\beta(6)\beta(7)$	$m_s = -1\frac{1}{2}$

Table V

Effects of the PI operations on the nuclear spin functions of identical atom sets

	E	(567) (576)	(56)* (67)* (57)*	(12)	(12)(567) (12)(576)	(12)(56)* (12)(67)* (12)(57)*	Species
$\alpha(1)\alpha(2)$	1	1	1	1	1	1	A'_1
$\alpha(1)\beta(2)$	1	1	1	0	0	0	$A'_1 + A''_1$
$\beta(1)\beta(2)$	1	1	1	1	1	1	A'_1
$\beta(1)\beta(2)$	1	1	1	1	1	1	A'_1
Direct sum	4	4	4	2	2	2	$3A'_1 + A''_1$
1.	1	1	1	1	1	1	A'_1
2.	1	0	0	1	0	0	
3.	1	0	0	1	0	0	$A'_1 + E'$
4.	1	0	1	1	0	1	
5.	1	0	0	1	0	0	
6.	1	0	0	1	0	0	$A'_1 + E'$
7.	1	0	1	1	0	1	
8.	1	1	1	1	1	1	A'_1
Direct sum	8	2	4	8	2	4	$4A'_1 + 2E'$

ii. The operations P change the sequences $\alpha\beta$ in the nuclear spin functions. The numbering of atoms in these sequences are unimportant, i.e. $\alpha_{(1)}\beta_{(2)}$ and $\alpha_{(2)}\beta_{(1)}$ are equivalent and indistinguishable.

iii. If the sequence $\alpha\beta$ does not change, $\chi = 1$, if it changes, $\chi = 0$.

The full representation of the nuclear spin functions Ψ_{ns} can be derived as a direct product of full representations of the two identical atom sets. The result is:

$$(3A'_1 + A''_1)\otimes(4A'_1 + 2E') = 12A'_1 + 4A''_1 + 6E' + 2E'' . \tag{9}$$

The direct products of the above irreducible representation and the species $\Gamma(\Psi_{riri})$ can be seen in Table VI with the obtained nuclear spin statistical weights. The results correspond to the ones published by Kręglewski [1].

Table VI

The representation of the products $\Psi_{riri}\Psi_{ns}$ and the nuclear spin statistical weights

$\Gamma(\Psi_{riri})$	$\Gamma(\Psi_{riri})\otimes\Gamma(\Psi_{ns})$	$\Gamma(\Psi_t)$	Statistical weights
A'_1	$12A'_1 + 4A''_1 + 6E' + 2E''$	A''_1, A''_2	4
A'_2	$12A'_2 + 4A''_2 + 6E' + 2E''$	A''_1, A''_2	4
A''_1	$12A''_1 + 4A'_1 + 6E'' + 2E'$	A''_1, A''_2	12
A''_2	$12A''_2 + 4A'_2 + 6E'' + 2E'$	A''_1, A''_2	12
E'	$2A''_2 + 18E' + 6E'' + 6A'_1 + 6A'_2 + 2A''_1$	A''_1, A''_2	4
E''	$2A'_2 + 18E'' + 6E' + 6A''_1 + 6A''_2 + 2A'_1$	A''_1, A''_2	12

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