

N₂-エチレンオキシド錯体の対称性

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Molecular Symmetry Group of N₂-Ethylene Oxide Complex

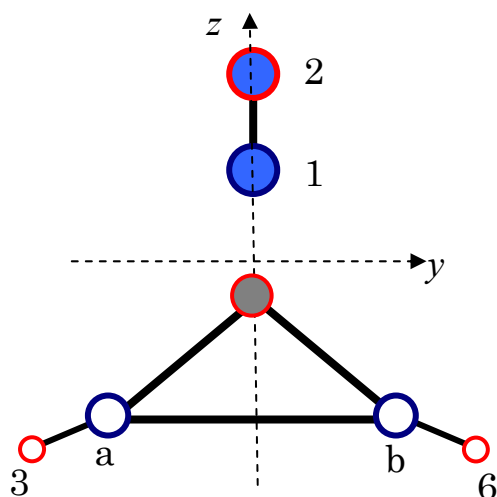
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The molecular symmetry group of N₂-ethylene oxide complex (N₂-EO) has been studied in order to understand the tunnel-rotation spectra observed by FTMW spectroscopy in KAIT. The group is composed of 8 operators, i.e. G₈, and thus a level splits into 8 components at most by tunneling. If the energy minimum structure of N₂-EO has C_s symmetry, it splits into 4.

1. Permutation-Inversion (PI) operations

Fig.1: C_s(I) type structure of N₂-EO

(The red circles for N, and O atoms,
Indicates that they are above the z-y plane.)



The structure at an energy minimum predicted for N₂-Ethylene oxide complex (N₂-EO) by *ab-initio* calculation is illustrated schematically in Fig. 1. This structure has the point group symmetry C_s, and we call this C_s(I) type. The molecular fixed z-axis connects the centers of mass of N₂ and EO moiety. The x-axis can be defined in the symmetry plane, and the y-axis to be normal to this plane. The figure shows the positions of atoms watched from the x-axis direction. Two nitrogen atoms are labeled by 1 and 2, two carbon atoms a and b, and four hydrogen atoms 3, 4, 5, and 6. C_aH₃H₅ forms one methylene group, and C_bH₄H₆ the other. The PI group for N₂-EO is formed by 8 feasible operators, as given in Table I, where

Table I. Character Table of G₈(N₂-EO)

G ₈ (N ₂ -EO)	E	O ₁	O ₂ *	O ₃ *	(12)	(12)O ₁	(12)O ₂ *	(12)O ₃ *
A _{1s}	1	1	1	1	1	1	1	1
A _{2s}	1	1	-1	-1	1	1	-1	-1
B _{1s}	1	-1	1	-1	1	-1	1	-1
B _{2s}	1	-1	-1	1	1	-1	-1	1
A _{1a}	1	1	1	1	-1	-1	-1	-1
A _{2a}	1	1	-1	-1	-1	-1	1	1
B _{1a}	1	-1	1	-1	-1	1	-1	1
B _{2a}	1	-1	-1	1	-1	1	1	-1

$O_1=(34)(56)(ab)$, $O_2^*=(36)(45)(ab)^*$, $O_3^*=(35)(46)^*$. The group is isomorphic with D_{2h} point group, and we call it $G_8(N_2\text{-EO})$.

2. Energy and symmetry of tunneling splitting

In case of $C_s(I)$ type, there are four equivalent energy minima in the potential energy surface as shown in Fig. 2. Energy splitting may be evaluated by Hougen's high barrier tunneling model. By introducing four wavefunctions localized at each minima, $\Psi_{rve}^0(i)$ ($i=I, \dots, IV$), we construct 4x4 matrix as

Localized state	(I)	(II)	(III)	(IV)
$\Psi_{rve}^0(I)$	E_0	w_{12}	w_{13}	$w_{14}=w_{23}$
$\Psi_{rve}^0(II)$		E_0	w_{23}	$w_{24}=w_{13}$
$\Psi_{rve}^0(III)$			E_0	$w_{34}=w_{12}$
$\Psi_{rve}^0(IV)$				E_0

where w_{ij} represents tunneling interaction matrix elements between the structure (i) and (j); see Fig. 2. This matrix can be easily diagonalized and we have four eigen values, eigen states and their symmetry as, $[E_0+w_{12}+w_{13}+w_{23}, \Psi_{rve}^0(++++), A_{1s}]$, $[E_0-w_{12}+w_{13}-w_{23}, \Psi_{rve}^0(+++-), B_{1s}]$, $[E_0+w_{12}-w_{13}-w_{23}, \Psi_{rve}^0(++--), A_{1a}]$, and $[E_0-w_{12}-w_{13}+w_{23}, \Psi_{rve}^0(+--+), B_{1a}]$.

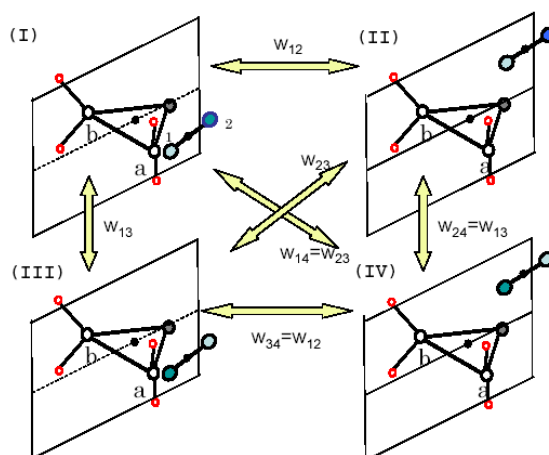


Fig. 2: Four energy minima in $C_s(I)$ typ

3. Symmetry of rotational wavefunctions

The symmetry of the rotational wavefunctions can be obtained by inspecting equivalent rotations for each symmetry operations of $G_8(N_2\text{-EO})$. The molecule-fixed axis system, or complex-fixed in the present case, should be defined for this. We found that we can introduce at least two different definitions of molecule-fixed axis system for the $N_2\text{-EO}$ complex, and thus two different symmetry classifications are possible for a rotational state $|J, K_a, K_c\rangle$,

4. In the presentation, the nature of the observed tunnel-rotation spectra will be discussed from the viewpoint of molecular symmetry together with selection rules and nuclear spin statistics.