Effect of Phase Choices in Rovibrational Wavefunctions on the Labeling of K- and *l*-Type Doubling in Molecular Energy Levels

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The change in phase factor of the wavefunction does not affect the absolute value of the matrix element, but does change the phase factor of the off-diagonal matrix element. This phase dependence causes a serious confusion in the sign of some parameters in the molecular Hamiltonian, which appear only in the off-diagonal matrix element; for example, the sign of the *l*-type doubling constant q of a linear or a symmetric-top molecule. In the present paper, the energy eigenvalues, symmetry species, and labeling of the eigenfunctions are discussed for the K-type doubling of asymmetric-top molecules and for the *l*-type doubling of linear or symmetric-top molecules in relation to the choices of phases in the basis wavefunctions.

I. Introduction

A glance at the literature for linear and symmetric top molecules shows an annoying confusion of plus and minus signs accompanying the *l*-type doubling constant q. For example: the q constants for acetylene were reported as positive by Lafferty, Suenram, and Johnson [1] and Matsumura, Tanaka, Endo, Saito, and Hirota [2], but on the other hand Strey and Mills [3] and Pliva [4] reported negative q values. For asymmetric tops, confusion is seen in the association of symmetry species labels with Wang submatrix labels of individual levels. Equations (24.8) or Table 7 in Nielsen's article [5], for instance, are not consistent with Eqs. (1) or Table 2n1 in Sect. 2n of Allen and Cross's book [6]. The origin of all of these problems is the choice of phase factors in wavefunctions.

In the present paper, it is shown in this section why the phase factor is critical for the problems. In Sects. II – V the origin of the "arbitrary" phase factor is reviewed. The phase factor is followed through the general transformation properties of the symmetric-top wavefunctions, and it is shown how the definition of the Wang linear combinations limits the phase factor to a discrete range of values. The remaining "arbitrary" choices are compared for an asymmetric rotor. In Sects. VI – VIII a similar treatment is followed for linear molecules. In Sect. IX brief comment will be given for symmetric tops.

The arbitrary phase factor arises from the fact that the Schrödinger equation is homogeneous in the wavefunction,

$$\hat{H}\,\psi_n = E_n\,\psi_n\,. \qquad (1)$$

The energy eigenvalue E_n is independent of the amplitude of the wavefunction. The amplitude of the wavefunction may be defined by normalization of the wavefunction. However, the eigenfunction thus defined still has an arbitrary phase factor, because the amplitude of the wavefunction can be a complex quantity.

Now we look at the matrix elements of a perturbing operator $\hat{H}'$. By changing the phase of the wavefunction ψ_n by α_n, a new wavefunction ψ'_n is obtained:

$$\psi'_n = \exp[i\,\alpha_n]\,\psi_n\,. \qquad (2)$$

Using these new wavefunctions as the basis set, the matrix elements of $\hat{H}'$ can be obtained. They are related to those in the old basis set by

$$\langle\psi'_n|\hat{H}'|\psi'_m\rangle = \exp[i(\alpha_m-\alpha_n)]\langle\psi_n|\hat{H}'|\psi_m\rangle\,. \qquad (3)$$

This equation shows that the change in phase factor of the wavefunction does not affect the absolute value of the matrix element, but does change the phase factor of the matrix element. It should be noted that only the relative phase of the two wavefunctions appears in the right side of (3). The diagonal matrix elements are not changed at all by the phase choices because the phase factor in (3) vanishes if $n = m$.

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When the two states, n and m, are degenerate with a common eigenvalue E, the off-diagonal matrix element of the perturbing term between the two states contributes directly to the energy, and the phase factor plays an important role. For a two level system the energy matrix is given as

$$\begin{array}{c} \psi_n \\ \psi_m \end{array} \begin{bmatrix} E & H'_{nm} \\ H'^{*}_{nm} & E \end{bmatrix} . \tag{5}$$

This energy matrix can be diagonalized by taking linear combinations of the wavefunctions. If the off-diagonal matrix element H'_{nm} is real, we may take $\psi^+ = (\psi_n + \psi_m)/\sqrt{2}$ and $\psi^- = (\psi_n - \psi_m)/\sqrt{2}$, and obtain

$$\begin{array}{c} \psi^+ \\ \psi^- \end{array} \begin{bmatrix} E + H'_{nm} & 0 \\ 0 & E - H'_{nm} \end{bmatrix} . \tag{6}$$

The off-diagonal element appears in the eigenvalues, which now contain the contribution of the phases. The energies of the ψ^+ and ψ^- states depend on the phase choices in the original basis functions. This is the case for K-type doubling of the $K = 1$ state of an asymmetric rotor and l-type doubling of the $|l| = 1$ state of a linear or symmetric-top molecule.

The intent of this paper is to make this phase dependence clear by following the standard theory but emphasizing the phase factor in all steps. The notations and formulations follow closely the book of Bunker [7].

II. Symmetric-Top Wavefunction

The eigenfunction for rotation of a symmetric top is usually called a symmetric-top wavefunction, which is the eigenfunction of the following rotational Hamiltonian:

$$\hat{H}_{\mathrm{sym}} = [A\hat{J}_z^2 + B(\hat{J}_x^2 + \hat{J}_y^2)]/\hbar^2 , \tag{7}$$

where $\hat{J}_x$, $\hat{J}_y$, and $\hat{J}_z$ are the angular momentum operators in the molecule-fixed axis system, and A and B are the rotational constants in units of energy. The z axis is the axis of symmetry, and we assume here that the top is prolate, $A > B$. This assumption does not limit the generality of the following discussion.

By introducing the Euler angles, Fig. 1, the Hamiltonian operator (7) can be written in the differential operator form, and the following Schrödinger equation is obtained:

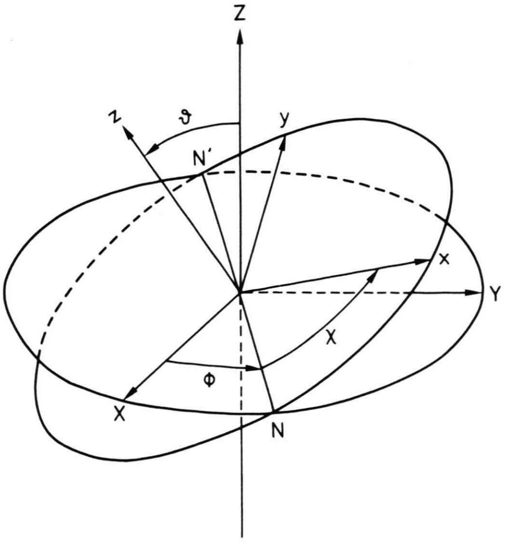

Fig. 1. Definition of the Euler angles.

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2} + \left(\frac{\cos^2\theta}{\sin^2\theta} + \frac{A}{B}\right)\frac{\partial^2\psi}{\partial\chi^2} - \frac{2\cos\theta}{\sin^2\theta}\frac{\partial^2\psi}{\partial\chi\,\partial\varphi} + \frac{E}{B}\psi = 0 . \tag{8}$$

The definition of the Euler angles is the same as that of Van Winter [8], Herzberg [9], Landau and Lifshitz [10], Townes and Schawlow [11], and Gordy and Cook [12]. However unfortunately this definition is not the same as that of Bunker [7], Edmonds [13], Nielsen [5], and Wilson, Decius, and Cross [14]. The differences between these two definitions of the Euler angles are in the definitions of φ and χ. The former uses the angles $(X-0-N)$ and $(x-0-N)$, and the latter uses the angles $(Y-0-N)$ and $(y-0-N)$ for φ and χ, respectively. Therefore φ and χ differ by $\pi/2$ in the two definitions. However the Schrödiger equation (8), is the same for both definitions of the angles, because the variables φ and χ appear only in the differential operators.

The eigenfunction of (8) is written as

$$\psi = S_{Jkm}(\theta)\exp[i\,m\,\varphi]\exp[i\,k\,\chi] . \tag{9}$$

Since the different definitions of the Euler angles shift the angles φ and χ by $\pi/2$, the eigenfunction (9) changes its phase factor when the angle definition is changed. The change of phase is thus dependent on the quantum numbers m and k. However, since the phase is "arbitrary", it can be ultimately defined in either case by using the off-diagonal matrix elements as discussed later.

The eigenfunction (9) is simultaneously the eigenfunction of the angular momentum operators $\hat{J}^2$, $\hat{J}_Z$, and $\hat{J}_z$;

$$\hat{J}^2 \psi = \hbar^2 J(J+1)\psi, \quad \hat{J}_Z \psi = \hbar m \psi,$$

and

$$\hat{J}_z \psi = \hbar k \psi, \tag{10}$$

where the subscript Z means space-fixed Z axis, and that of z means molecule-fixed z axis. Thus we express the wavefunction by these three quantum numbers J, k, and m;

$$\psi = |J, k, m\rangle. \tag{11}$$

The quantum numbers k and m can have $2J+1$ values, from $-J$ to $+J$. Later we use the capital letters K and M for the absolute values of k and m, respectively. The functions $|J, 0, m\rangle$ are proportional to the spherical harmonics which are the eigenfunctions of a diatomic molecular rotator.

In most papers, the phase factors are given in this step with full mathematical expressions of the functions $|J, k, m\rangle$, for example see [8]. However we introduce the phase factor in a different way, because it is much more convenient to define the relative phases of the wavefunctions by using the off-diagonal matrix elements. In the next section it is shown how to define the phase of the function $|J, k, m\rangle$ relative to the function $|J, 0, 0\rangle$,

$$|J, 0, 0\rangle = N \frac{\mathrm{d}^J}{\mathrm{d}(\cos\theta)^J}(\cos^2\theta - 1)^J, \tag{12}$$

where N is a normalization constant.

III. Building up the Function $|J, k, m\rangle$

The ladder operators for the symmetric-top wavefunctions are defined by

$$\hat{J}_\mathrm{r}^\pm = \hat{J}_x \pm i\hat{J}_y, \quad \hat{J}_\mathrm{s}^\pm = \hat{J}_X \pm i\hat{J}_Y, \tag{13}$$

where the subscript r means that the operators are defined in the rotating axis system which is fixed in the molecule, and the subscript s means that the operators are defined in the space-fixed axis system. The matrix elements of these ladder operators can be found in any textbook:

$$\langle J, k, m | \hat{J}_\mathrm{s}^+ | J, k, m-1\rangle = f(J, m)\exp(-i\sigma),$$
$$\langle J, k, m-1 | \hat{J}_\mathrm{s}^- | J, k, m\rangle = f(J, m)\exp(i\sigma), \tag{14}$$

$$\langle J, k-1, m | \hat{J}_\mathrm{r}^+ | J, k, m\rangle = f(J, k)\exp(i\varrho),$$
$$\langle J, k, m | \hat{J}_\mathrm{r}^- | J, k-1, m\rangle = f(J, k)\exp(-i\varrho), \tag{15}$$

where

$$f(J, n) = \hbar[J(J+1) - n(n-1)]^{1/2}. \tag{16}$$

Here we have introduced the phases σ and ϱ, which represent the phase differences of the two wavefunctions used for calculating the matrix elements. In most textbooks, these phase factors are assumed in an *a priori* manner to be 1, -1, i, or $-i$. In the present work we take a more general approach. The phase factors are written explicitly and we have them in so that their effect is seen in the final equations. Since the quantity σ and ϱ are "arbitrary", these quantities can be functions of the quantum numbers. However such a choice of phases is not practical, and we will assume that σ and ϱ are constant. This assumption does not harm the generality in the following discussion.

Because of the hermitian properties of the angular momentum operators, the two matrix elements in (14) should be each other's complex conjugate, and the same is true for the matrix elements in (15). Therefore the phase factors in (14) are related; one has σ and the other has $-\sigma$ as the phase. In (15), one has the phase of ϱ and the other $-\varrho$.

Equations (14) can be rewritten as

$$|J, k, m+1\rangle = \exp[i\sigma]\hat{J}_\mathrm{s}^+ |J, k, m\rangle / f(J, m+1)$$

and

$$|J, k, m-1\rangle = \exp[-i\sigma]\hat{J}_\mathrm{s}^- |J, k, m\rangle / f(J, m). \tag{17}$$

Using these equations M times successively, starting with the function $|J, k, 0\rangle$, we obtain

$$|J, k, M\rangle = \hbar^{-M}\exp[iM\sigma][(J-M)!/(J+M)!]^{1/2} \cdot (\hat{J}_\mathrm{s}^+)^M |J, k, 0\rangle$$

and

$$|J, k, -M\rangle = \hbar^{-M}\exp[-iM\sigma][(J-M)!/(J+M)!]^{1/2} \cdot (\hat{J}_\mathrm{s}^-)^M |J, k, 0\rangle. \tag{18}$$

In a similar manner the wavefunctions $|J, K, m\rangle$ can be created from the function $|J, 0, m\rangle$ by applying the $\hat{J}_\mathrm{r}^{\pm}$ operator K times;

$$|J, K, m\rangle = \hbar^{-K} \exp[i K \varrho] [(J-K)!/(J+K)!]^{1/2} \cdot (\hat{J}_\mathrm{r}^{-})^K |J, 0, m\rangle ,$$

and

$$|J, -K, m\rangle = \hbar^{-K} \exp[-i K \varrho] [(J-K)!/(J+K)!]^{1/2} \cdot (\hat{J}_\mathrm{r}^{+})^K |J, 0, m\rangle . \tag{19}$$

By combining these four equations, (18) and (19), we have

$$|J, \pm K, (\pm) M\rangle = \hbar^{-K-M} \exp[\pm i K \varrho] \exp[(\pm) i M \sigma] \cdot [(J-K)!(J-M)!/(J+K)!(J+M)!]^{1/2} \cdot (\hat{J}_\mathrm{r}^{\mp})^K (\hat{J}_\mathrm{s}^{(\pm)})^M |J, 0, 0\rangle , \tag{20}$$

where the ± signs are correlated with each other and the (±) signs are also correlated with each other. Each of the symmetric-top wavefunctions thus generated has a unique phase which is defined by the phase factors in the matrix elements of the ladder operators in (14) and (15).

Now we define the normalization factor, which includes the phase factor, of the wavefunction $|J, \pm K, (\pm) M\rangle$ as

$$N_{J, \pm K, (\pm) M} = \hbar^{-M-K} \exp[\pm i K \varrho] \exp[(\pm) i M \sigma] \cdot \{(J-K)!(J-M)!/(J+K)!(J+M)!\}^{1/2} . \tag{21}$$

We have then a relation

$$N_{J, K, m} = N_{J, -K, m} \exp[2 i K \varrho] \tag{22}$$

which is used in the next section.

IV. Symmetry Properties of the Symmetric-Top Wavefunction

Following Bunker [7] we introduce two operators; one rotates the molecule-fixed axes by an angle β about the z axis, R_z^β, and the other rotates the molecule-fixed axes by π about an axis which is in the $x-y$ plane and which is α radians from the x axis, R_α^π. The transformation properties of the Euler angles and angular momentum components in the molecule-fixed axis system are summarized in Table 1, which is identical to Table 7-1 of Bunker's book except for the property of χ for the R_α^π operation. The difference arises from the different definition of the Euler angles.

Table 1. Transformation properties of the Euler angles and angular momentum.

	R_z^β	R_α^π
θ	θ	$\pi - \theta$
φ	φ	$\varphi + \pi$
χ	$\chi + \beta$	$\pi - \chi - 2\alpha$
$\hat{J}_x$	$\hat{J}_x \cos\beta + \hat{J}_y \sin\beta$	$\hat{J}_x \cos 2\alpha + \hat{J}_y \sin 2\alpha$
$\hat{J}_y$	$\hat{J}_y \cos\beta + \hat{J}_x \sin\beta$	$-\hat{J}_y \cos 2\alpha + \hat{J}_x \sin 2\alpha$
$\hat{J}_z$	$\hat{J}_z$	$-\hat{J}_z$

From the transformation properties of the Euler angles, it can be shown that the wavefunction $|J, 0, 0\rangle$ is transformed by the two operators as

$$R_z^\beta |J, 0, 0\rangle = |J, 0, 0\rangle \tag{23}$$

and

$$R_\alpha^\pi |J, 0, 0\rangle = (-1)^J |J, 0, 0\rangle . \tag{24}$$

From the transformation properties of the angular momentum operators, the following operator equations can be obtained:

$$R_z^\beta \hat{J}_\mathrm{r}^{\pm} = \exp[\mp i \beta] \hat{J}_\mathrm{r}^{\pm} R_z^\beta \tag{25}$$

and

$$R_\alpha^\pi \hat{J}_\mathrm{r}^{\pm} = \exp[\pm 2 i \alpha] \hat{J}_\mathrm{r}^{\mp} R_\alpha^\pi . \tag{26}$$

Since the operators R_z^β and R_α^π do not change anything about the space-fixed axes, they commute with the $\hat{J}_\mathrm{s}^{\pm}$ operators. By using these equations, (23–26), the transformation properties of the symmetric top wavefunctions $|J, k, m\rangle$ can be obtained as

$$R_z^\beta |J, \pm K, (\pm) M\rangle = R_z^\beta N_{J, \pm K, (\pm) M} \cdot (\hat{J}_\mathrm{r}^{\mp})^K (\hat{J}_\mathrm{s}^{(\pm)})^M |J, 0, 0\rangle \tag{27}$$
$$= \exp[\pm i K \beta] |J, \pm K, (\pm) M\rangle ,$$

$$R_\alpha^\pi |J, \pm K, (\pm) M\rangle = R_\alpha^\pi N_{J, \pm K, (\pm) M} \cdot (\hat{J}_\mathrm{r}^{\mp})^K (\hat{J}_\mathrm{s}^{(\pm)})^M |J, 0, 0\rangle$$
$$= (-1)^J \exp[\mp 2 i K \alpha] N_{J, \pm K, (\pm) M} \cdot (\hat{J}_\mathrm{r}^{\pm})^K (\hat{J}_\mathrm{s}^{(\pm)})^M |J, 0, 0\rangle . \tag{28}$$

Equation (28) can be rewritten by using the relation between the normalization factors, (22), as

$$R_\alpha^\pi |J, \pm K, (\pm) M\rangle = (-1)^J \exp[\mp 2 i K \alpha] N_{J, \pm K, (\pm) M} \cdot |J, \mp K, (\pm) M\rangle / N_{J, \mp K, (\pm) M} \tag{29}$$
$$= (-1)^J \exp[\mp 2 i K \alpha] \exp[\pm 2 i K \varrho] \cdot |J, \mp K, (\pm) M\rangle .$$

Equations (27) and (29) can be summarized in more general form:

$$R_z^{\beta}|J,k,m\rangle = \exp[ik\beta]|J,k,m\rangle$$

and

$$R_\alpha^{\pi}|J,k,m\rangle = (-1)^J \exp[-2ik\alpha] \cdot \exp[2ik\varrho]|J,-k,m\rangle. \quad (30)$$

It should be noted that the transformation properties of the symmetric top wavefunctions depend on the "arbitrary" phase, ϱ.

V. Wang Linear Combinations and K-type Doubling

The rotational Hamiltonian of an asymmetric top is

$$\hat{H}_{\text{asym}} = [A\hat{J}_a^2 + B\hat{J}_b^2 + C\hat{J}_c^2]/\hbar^2, \quad (31)$$

which can be rewritten by using the ladder operators as

$$\hat{H}_{\text{asym}} = \{[A-(B+C)/2]\hat{J}_z^2 + (B+C)\hat{J}^2/2 + (B-C)[(\hat{J}_r^+)^2 + (\hat{J}_r^-)^2]/4\}/\hbar^2, \quad (32)$$

where we used the I^r representation [15] for the molecule-fixed axes; the axis of the smallest moment of inertia, a, is the z axis, the axis for the largest moment of inertia, c, is the y axis, and the b axis is thus the x axis. If we neglect the last term in the Hamiltonian (32), the Hamiltonian is identical to that of a symmetric rotor. Therefore we can use the symmetric top wavefunctions as the basis set for the asymmetric rotor wavefunctions. The term with $(B-C)$ gives off-diagonal matrix elements in this basis. The Hamiltonian (31) shows that it is invariant under the symmetry operations of the four-group [16], $\{E, R_x^{\pi}, R_y^{\pi}, R_z^{\pi}\}$. Therefore it is best to have a basis set which forms the irreducible representation of this group. The Wang transformation [17] is used for this purpose. The character table of the four-group V is given in Table 2.

Table 2. Character table of four-group V.

V	E	R_z^{π}	R_x^{π}	R_y^{π}
A	1	1	1	1
B_z	1	1	−1	−1
B_x	1	−1	1	−1
B_y	1	−1	−1	1

The Wang linear combinations are defined for $K \neq 0$ as

$$|J,K,m,\gamma\rangle = [|J,K,m\rangle + (-1)^{\gamma}|J,-K,m\rangle]/\sqrt{2}, \quad (33)$$

where γ is an even or odd integer, or simply 0 or 1. They are required to form a basis set of an irreducible representation of the four-group. Since the three rotational operators in group V are special cases of R_z^{β} and R_α^{π}, the following transformation properties of the symmetric-top wavefunctions can be derived using (30):

$$R_x^{\pi}|J,k,m\rangle = (-1)^J \exp[2ik\varrho]|J,-k,m\rangle,$$

$$R_y^{\pi}|J,k,m\rangle = (-1)^{J+k} \exp[2ik\varrho]|J,-k,m\rangle,$$

and

$$R_z^{\pi}|J,k,m\rangle = (-1)^k|J,k,m\rangle. \quad (34)$$

The Wang linear combinations are then transformed as

$$R_x^{\pi}|J,K,m,\gamma\rangle = (-1)^{J+\gamma}\exp[-2iK\varrho] \cdot \{|J,K,m\rangle + (-1)^{\gamma}\exp[4iK\varrho]|J,-K,m\rangle\}/\sqrt{2},$$

$$R_y^{\pi}|J,K,m,\gamma\rangle = (-1)^{J+K+\gamma}\exp[-2iK\varrho] \cdot \{|J,K,m\rangle + (-1)^{\gamma}\exp[4iK\varrho]|J,-K,m\rangle\}/\sqrt{2},$$

$$R_z^{\pi}|J,K,m,\gamma\rangle = (-1)^K|J,K,m,\gamma\rangle. \quad (35)$$

Two of the above relations include the "arbitrary" phase ϱ. Here we come to an important result: The Wang linear combinations defined by (33) can form a basis set for the irreducible representation of the four-group only when the "arbitrary" phases of the symmetric top wavefunctions are chosen so that

$$\exp[4iK\varrho] = 1, \quad \text{or} \quad \varrho = n\pi/2, \quad (36)$$

so that the right hand sides of (35) are proportional to the original function $|J,K,m,\gamma\rangle$. If some other phase choice is used in the symmetric top wavefunctions we have to use linear combinations with complex coefficients instead of the simple form of (33). More generally, we can state that the choice of phase is not "arbitrary" any more if we require certain symmetry properties for the wavefunctions [8, 15].

In the choice of phase in (36), the transformation properties of the Wang linear combinations are as follows: for the phase choice (i) $n =$ even integer ($\varrho = 0, \pi, \ldots$),

$$R_x^{\pi}|J,K,m,\gamma\rangle = (-1)^{J+\gamma}|J,K,m,\gamma\rangle,$$

$$R_y^{\pi}|J,K,m,\gamma\rangle = (-1)^{J+K+\gamma}|J,K,m,\gamma\rangle,$$

Table 3. Four-group symmetry of Wang linear combination.

			even J		odd J	
	K	γ	(i) $\varrho = 0, \pi$	(ii) $\varrho = \pi/2, 3\pi/2$	(i) $\varrho = 0, \pi$	(ii) $\varrho = \pi/2, 3\pi/2$
E^+	e	e	A	A	B_z	B_z
E^-	e	o	B_z	B_z	A	A
0^+	o	e	B_x	B_y	B_y	B_x
0^-	o	o	B_y	B_x	B_x	B_y

and

$$R_z^\pi |J, K, m, \gamma) = (-1)^K |J, K, m, \gamma), \tag{37}$$

and for the phase choice (ii) $n =$ odd integer ($\varrho = \pi/2, 3\pi/2, \ldots$),

$$R_x^\pi |J, K, m, \gamma) = (-1)^{J+K+\gamma} |J, K, m, \gamma),$$

$$R_y^\pi |J, K, m, \gamma) = (-1)^{J+\gamma} |J, K, m, \gamma),$$

and

$$R_z^\pi |J, K, m, \gamma) = (-1)^K |J, K, m, \gamma). \tag{38}$$

It should be noted here that the characters of R_x^π and R_y^π are interchanged if we change the phase choice (i) to (ii). For example, Nielsen [5] used the former phase convention and Allen and Cross [6] used the latter.

For a given J, the symmetry of the Wang linear combination is represented by the parities of K and γ. The wavefunctions are then labelled as E^+, E^-, O^+, and O^- [15], where E and O represent $K =$ even and odd state respectively, and + and − represent $\gamma =$ even and odd combinations in (33) respectively. The symmetry properties of the Wang linear combination are summarized in Table 3. The most important effect of the choice of phase is that the symmetry of the O^+ and O^- wavefunctions are opposite for choice (i) and (ii). In Table 3 and the following, the range of the phase choice is represented by 0, $\pi/2$, π, $3\pi/2$, instead of the general form of (36).

The diagonal matrix element for $K = 1$ using Wang linear combinations as the basis is

$$\begin{aligned}(J, 1, m, \gamma | \hat{H}_{\text{asym}} | J, 1, m, \gamma) &= A - (B + C)/2 + (B + C)J(J + 1)/2 \\ &\quad + (-1)^\gamma \cos(2\varrho)(B - C)J(J + 1)/4 .\end{aligned} \tag{39}$$

The off-diagonal element between $\gamma =$ even and $\gamma' =$ odd states is

$$\begin{aligned}(J, 1, m, \gamma | \hat{H}_{\text{asym}} | J, 1, m, \gamma') &= -i \sin(2\varrho)(B - C)J(J + 1)/4 ,\end{aligned} \tag{40}$$

which is purely imaginary, and vanishes in any of the choices of phase in (36). This fact corresponds to that mentioned in the introduction, (5) and (6). In the present choice of phase, the off-diagonal matrix elements of the asymmetric rotor Hamiltonian $\hat{H}_{\text{asym}}$ in the basis of symmetric top wavefunctions are all real, and the energy matrix for $k = 1$ and -1 states can be diagonalized by the Wang linear combinations. This is a direct result of the fact that we required the four-group symmetry of the Wang linear combinations: off-diagonal matrix elements vanish between states of different symmetry.

Thus, (39) represents the rotational energy of the $K = 1$ states of the asymmetric rotor in the first order approximation. In the phase choice (i), $\varrho = 0$ or π, the matrix element is

$$\begin{aligned}(J, 1, m, \gamma | \hat{H}_{\text{asym}} | J, 1, m, \gamma) &= A - (B + C)/2 + (B + C)J(J + 1)/2 \\ &\quad + (-1)^\gamma (B - C)J(J + 1)/4 .\end{aligned} \tag{41}$$

This equation shows that the O^+ component of the $K = 1$ doublet has higher energy than the O^- component. In the phase choice (ii), $\varrho = \pi/2$ or $3\pi/2$, the matrix element is

$$\begin{aligned}(J, 1, m, \gamma | H_{\text{asym}} | J, 1, m, \gamma) &= A - (B + C)/2 + (B + C)J(J + 1)/2 \\ &\quad - (-1)^\gamma (B - C)J(J + 1)/4 ,\end{aligned} \tag{42}$$

which shows that the O^+ component of the $K = 1$ doublet has *lower* energy than the O^- component. Thus the correspondence between O^+ and O^- wavefunctions and the upper and lower components of a $K = 1$ doublet is inverted by the change of phase choice. However, since the phase choice also reverses the symmetry of the O^+ and O^- wavefunctions as seen above, the upper $K = 1$ component always has B_x symmetry and the lower has B_y symmetry. This relation is invariant under the change of phase

Table 4. Classification of wavefunctions of K-doubling components for $K = 1$ of an Asymmetric rotor.

K-doubling component	Symmetry for even J state	Wavefunction with phase choice	
		(i) $\varrho = 0, \pi$	(ii) $\varrho = \pi/2, 3\pi/2$
upper	B_x	O^+	O^-
lower	B_y	O^-	O^+

choice. It is reasonable because the eigenvalue or character of a non-degenerate state is defined by a homogeneous equation of a linear operator, like the Schrödinger equation (1), which does not depend on the phase factor of the wavefunction. These results are summarized in Table 4.

VI. Two Dimensional Isotropic Harmonic Oscillator

A bending vibration of a linear molecule is described as a two dimensional isotropic harmonic oscillator (THO) in the zero-order approximation. Such a bending vibration is doubly degenerate and the Hamiltonian is given by

$$\hat{H}_{\mathrm{THO}} = [(\hat{P}_a^2 + \hat{P}_b^2)/m + f(R_a^2 + R_b^2)]/2\,, \qquad (43)$$

where R_a and R_b are the two displacement coordinates of the degenerate bending mode, $\hat{P}_a$ and $\hat{P}_b$ are the conjugate momenta, m is the reduced mass, and f is the force constant. It is convenient to introduce dimensionless coordinates [5] defined as

$$q_a = \lambda^{1/4}(m/\hbar)^{1/2} R_a$$

and

$$q_b = \lambda^{1/4}(m/\hbar)^{1/2} R_b\,, \qquad (44)$$

where $\lambda = f/m$. Then the THO Hamiltonian is expressed by these new coordinates and conjugate momenta as

$$\hat{H}_{\mathrm{THO}} = \hbar\,\omega\,(\hat{p}_a^2/\hbar^2 + \hat{p}_b^2/\hbar^2 + q_a^2 + q_b^2)/2\,, \qquad (45)$$

where $\omega = \lambda^{1/2}$ is called the harmonic frequency (radian/s). Using cylindrical coordinates, the coordinates q_a and q_b are

$$q_a = q\cos\alpha \quad \text{and} \quad q_b = q\sin\alpha\,, \qquad (46)$$

as shown in Fig. 2, where the angle α is measured from the molecule-fixed x axis. When the bending vibration is excited, an angular momentum is directed along the z axis, and is expressed by an operator $\hat{M}$,

$$\hat{M} = q_a\hat{p}_b - q_b\hat{p}_a\,, \qquad (47)$$

or in mathematical form using cylindrical coordinates,

$$\hat{M} = -i\hbar\,(\partial/\partial\alpha)\,. \qquad (48)$$

The eigenfunctions of the Hamiltonian (45) are

$$|v, l\rangle = F_{vl}(q)\exp[i\,l\,\alpha]\,, \qquad (49)$$

where

$$\hat{M}|v, l\rangle = l\hbar\,|v, l\rangle\,, \qquad (50)$$

and F_{vl} is a function of the scalar quantity q. The vibrational angular momentum quantum number can take $v + 1$ values, $-v$, $-v + 2, \ldots, 0$ or $1, \ldots, v - 2$, and v.

Now we introduce the ladder operator technique to build up the wavefunctions of the THO [7, 18]. First we define the following operators:

$$q^{\pm} = q_a \pm i\,q_b \quad \text{and} \quad \hat{p}^{\pm} = \hat{p}_a \pm i\,\hat{p}_b\,. \qquad (51)$$

Then four ladder operators are defined as

$$\hat{R}^{\pm(\pm)} = \hat{p}^{(\pm)}/\hbar \pm i\,q^{(\pm)}\,, \qquad (52)$$

where $\pm$ signs are correlated with each other and the $(\pm)$ signs are also correlated with each other. Using commutation relations,

$$[\hat{p}^{\pm}, q^{\pm}] = 0 \quad \text{and} \quad [\hat{p}^{\pm}, q^{\mp}] = -2\,i\,\hbar\,, \qquad (53)$$

it is shown that

$$[\hat{H}_{\mathrm{THO}}, \hat{R}^{\pm(\pm)}] = \pm\,\hbar\,\omega\,\hat{R}^{\pm(\pm)}$$

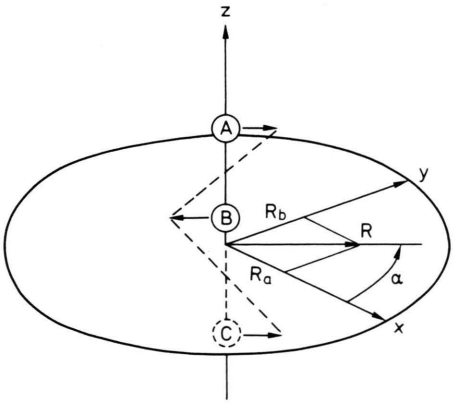

Fig. 2. Coordinates for the bending vibration in a linear ABC molecule.

and

$$[\hat{M}, \hat{R}^{\pm(\pm)}] = (\pm)\hbar\hat{R}^{\pm(\pm)}\,. \tag{54}$$

Equations (54) show that the operator $\hat{R}^{+(+)}$ is the ladder operator for $\Delta v = +1$ and $\Delta l = +1$, that $\hat{R}^{+(-)}$ is the ladder operator for $\Delta v = +1$ and $\Delta l = -1$, and so on. The matrix elements of these ladder operators can be evaluated using the relations

$$\hat{R}^{+(+)}\hat{R}^{-(-)} = 2\hat{H}_{\mathrm{THO}}/\hbar\omega + 2\hat{M}/\hbar - 2 \tag{55}$$

and

$$\hat{R}^{-(+)}\hat{R}^{+(-)} = 2\hat{H}_{\mathrm{THO}}/\hbar\omega - 2\hat{M}/\hbar + 2\,. \tag{56}$$

From (55) we obtain

$$\langle v, l|\hat{R}^{+(+)}\hat{R}^{-(-)}|v, l\rangle = 2(v+l)\,. \tag{57}$$

The left side of the equation can be rewritten as

$$\begin{aligned}&\langle v, l|\hat{R}^{+(+)}\hat{R}^{-(-)}|v, l\rangle\\ &= |\langle v, l|\hat{R}^{+(+)}|v-1, l-1\rangle|^2\\ &= |\langle v-1, l-1|\hat{R}^{-(-)}|v, l\rangle|^2\,,\end{aligned} \tag{58}$$

where a relation,

$$\begin{aligned}&\langle v, l|\hat{R}^{+(+)}|v-1, l-1\rangle\\ &= \langle v-1, l-1|\hat{R}^{-(-)}|v, l\rangle^*\,,\end{aligned} \tag{59}$$

was used, which is derived from the hermitian properties of the operator $\hat{p}$ and q. Then from (57) and (58) we have

$$\langle v, l|\hat{R}^{+(+)}|v-1, l-1\rangle = [2(v+l)]^{1/2}\exp[i\,\xi]\,, \tag{60}$$

where we assume that the arbitrary phase ξ is constant for all matrix elements as we have done in the case of symmetric-top wavefunctions. Similarly from (56) we obtain

$$\begin{aligned}&\langle v+1, l-1|\hat{R}^{+(-)}|v, l\rangle\\ &= [2(v-l+2)]^{1/2}\exp[i\,\eta]\,,\end{aligned} \tag{61}$$

where we use the relation

$$\begin{aligned}&\langle v, l|\hat{R}^{-(+)}|v+1, l-1\rangle\\ &= \langle v+1, l-1|\hat{R}^{+(-)}|v, l\rangle^*\,.\end{aligned} \tag{62}$$

The matrix elements of $\hat{R}^{-(-)}$ and $\hat{R}^{+(-)}$ operators can be obtained automatically by using (59) and (62).

Using (60) and (61) the eigenfunctions $|v, l\rangle$ can be generated from the totally symmetric function $|0, 0\rangle$. Equation (60) is rewritten as

$$\begin{aligned}|n+1, n+1\rangle = \exp[-i\,\xi]&\\ \cdot[4(n+1)]^{-1/2}\hat{R}^{+(+)}|n, n\rangle&\,.\end{aligned} \tag{63}$$

By successive use of this equation n times, starting from $|0, 0\rangle$, we obtain

$$\begin{aligned}|n, n\rangle = \exp[-i\,n\,\xi]\,2^{-n}(n!)^{-1/2}&\\ \cdot(\hat{R}^{+(+)})^n|0, 0\rangle&\,.\end{aligned} \tag{64}$$

Equation (61) is rewritten as

$$\begin{aligned}|n+p+1, n-(p+1)\rangle = \exp[-i\,\eta][4(p+1)]^{-1/2}&\\ \cdot\hat{R}^{+(-)}|n+p, n-p\rangle&\,.\end{aligned} \tag{65}$$

By successive use of this equation m times, starting with $|n, n\rangle$, we obtain

$$\begin{aligned}|n+m, n-m\rangle = \exp[-i\,m\,\eta]\,2^{-m}(m!)^{-1/2}&\\ \cdot(\hat{R}^{+(-)})^m|n, n\rangle&\,.\end{aligned} \tag{66}$$

Substituting (64) into (66), and changing the notation $n+m$ to v and $n-m$ to l, we have

$$|v, l\rangle = N_{v,l}(\hat{R}^{+(-)})^{(v-l)/2}(\hat{R}^{+(+)})^{(v+l)/2}|0, 0\rangle\,, \tag{67}$$

where the normalization factor $N_{v,l}$ is

$$\begin{aligned}N_{v,l} = \exp[-i(v+l)\,\xi/2 - i(v-l)\,\eta/2]&\\ \cdot 2^{-v}\{[(v+l)/2]!\,[(v-l)/2]!\}^{-1/2}&\,.\end{aligned} \tag{68}$$

Then a relation we use later may be shown to be

$$N_{v,l} = N_{v,-l}\exp[-i(\xi-\eta)\,l]\,. \tag{69}$$

VII. Symmetry Properties of Linear Molecule Wavefunctions

Before discussing the rovibrational wavefunctions of linear molecule, we will check the symmetry properties of the eigenfunctions of the two-dimensional isotropic harmonic oscillator under the molecular symmetry operations [7]. The common symmetry operation of all kinds of linear molecules is the inversion of the coordinates, E^*. The operation E^* is illustrated in Fig. 3 for a linear ABC molecule. It is easily seen that the transformation properties of the Euler angles are represented by the equivalent rotation R_y^π. Bunker [7] defined the molecule-fixed axes after the E^* operation in a different way; in his book the equivalent rotation of E^* is R_x^π. However, the present author prefers the definition of Fig. 3, because the equivalent rotation

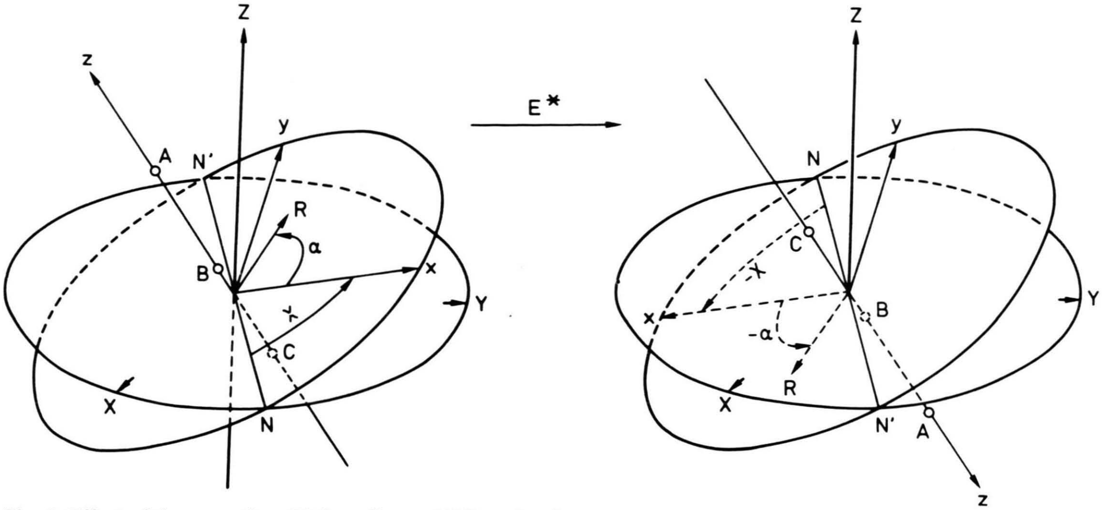

Fig. 3. Effect of the operation E^* for a linear ABC molecule.

of E^* for a very slightly bent ABC molecule is R_y^π in the I^r axis representation.

The Euler angle χ and the phase of the degenerate vibration α are transformed as

$$\chi \to -\chi, \quad \text{and} \quad \alpha \to -\alpha. \tag{70}$$

Then the operator $q^\pm$, which is

$$q^\pm = q \exp[\pm i\alpha] \tag{71}$$

is transformed by E^* as

$$q^\pm \to q^\mp ; \tag{72}$$

the amplitude q is a scalar quantity which is invariant under any symmetry transformation. Similarly we obtain

$$\hat{p}^\pm \to \hat{p}^\mp . \tag{73}$$

Using (72) and (73) we obtain the operator equations

$$E^* \hat{R}^{+(+)} = \hat{R}^{+(-)} E^*$$

and

$$E^* \hat{R}^{+(-)} = \hat{R}^{+(+)} E^* . \tag{74}$$

Operating with E^* on the both sides of (67), and using (74), we have

$$\begin{aligned} E^* |v, l\rangle &= N_{v,l} E^* (\hat{R}^{+(-)})^{(v-l)/2} (\hat{R}^{+(+)})^{(v+l)/2} |0, 0\rangle \\ &= N_{v,l} (\hat{R}^{+(+)})^{(v-l)/2} (\hat{R}^{+(-)})^{(v+l)/2} E^* |0, 0\rangle \\ &= N_{v,l} (\hat{R}^{+(+)})^{(v-l)/2} (\hat{R}^{+(-)})^{(v+l)/2} |0, 0\rangle , \end{aligned} \tag{75}$$

where we have used the transformation

$$E^* |0, 0\rangle = |0, 0\rangle . \tag{76}$$

Then using (69) we have

$$E^* |v, l\rangle = \exp[-i(\xi - \eta) l] \, |v, -l\rangle . \tag{77}$$

The rovibrational wavefunction of a symmetric-top molecule is a product of the symmetric-top wavefunction and the vibrational wavefunction,

$$\psi = |J, k, m\rangle |v_s, v_t, l_t\rangle , \tag{78}$$

where v_s represents all non-degenerate vibrations, and v_t represents all doubly degenerate vibrations, which are described by the eigenfunctions of THO Hamiltonian discussed above. If we select the functions which satisfy the relation

$$k = \sum_t l_t = l , \tag{79}$$

from the rovibrational wavefunctions of a symmetric top molecule, we have a basis set for a linear molecule [7]. Although these wavefunctions contain a redundant angle coordinate, they form a complete basis set of a linear molecule with the restriction of (79). They are

$$|J, l, m, v_s, v_t, l_t\rangle = |J, l, m\rangle |v_s, v_t, l_t\rangle . \tag{80}$$

Since the transformation properties of the symmetric top wavefunction $|J, k, m\rangle$ are known, and since the transformation properties of the THO wavefunctions are known, we can obtain the transformation properties of the linear molecule basis function;

$$\begin{aligned} E^* \lvert J, l, v_s, v_t, l_t\rangle &= (-1)^{J+l} \exp[2 i \varrho l] \\ &\quad \cdot \exp[-i \delta l] \lvert J, -l, m, v_s, v_t, -l_t\rangle , \end{aligned} \tag{81}$$

where we have used the fact that the wavefunctions for the stretching vibrations are symmetric under the E^* operation, and where we have assumed that the phase differences $\xi_t - \eta_t$ are the same for all bending vibrations

$$\delta = \xi_t - \eta_t . \tag{82}$$

Now we look at the case of a triatomic linear molecule, where only one bending mode exists. The discussion is much simpler in this case: the wavefunction can be represented by $\lvert J, l, m, v_1, v_2, v_3\rangle$ where v_2 is the bending mode as usual; in short $\lvert J, l, v\rangle$. Then we can define Wang-type linear combinations for $l \neq 0$, which form a basis set for the irreducible representation of the group $\{E, E^*\}$:

$$\begin{aligned} \lvert J, \lvert l\rvert, v, \gamma) = \{\lvert J, \lvert l\rvert, v\rangle \\ + (-1)^{\gamma} \lvert J, -\lvert l\rvert, v\rangle\}/\sqrt{2} . \end{aligned} \tag{83}$$

From (81) we obtain

$$\begin{aligned} E^* \lvert J, \lvert l\rvert, v, \gamma) &= (-1)^{J+l+\gamma} \exp[-i(2\varrho - \delta) l] \\ &\quad \cdot \{\lvert J, \lvert l\rvert, v\rangle + (-1)^{\gamma} \exp[-2i(2\varrho - \delta) l] \\ &\quad \cdot \lvert J, -\lvert l\rvert, v\rangle\}/\sqrt{2} . \end{aligned} \tag{84}$$

As we have seen in the Wang linear combinations for the asymmetric top, a special choice of phase is required for making the linear combination (83) form a basis set of the irreducible representation. That is

$$\exp[-2i(2\varrho - \delta) l] = 1 , \quad \text{or} \quad 2\varrho - \delta = n\pi . \tag{85}$$

If we keep the phase choice limitation of ϱ which is obtained in (36), we can conclude that the phase choice

$$\delta = n\pi \tag{86}$$

is required. Although there are many combinations of ϱ and δ fulfilling (36) and (86), the choice of phase can be grouped into two cases: for the phase choice (i) $2\varrho - \delta = 0$,

$$E^* \lvert J, \lvert l\rvert, v, \gamma) = (-1)^{J+l+\gamma} \lvert J, \lvert l\rvert, v, \gamma) , \tag{87}$$

and for the phase choice (ii) $2\varrho - \delta = \pi$,

$$E^* \lvert J, \lvert l\rvert, v, \gamma) = (-1)^{J+\gamma} \lvert J, \lvert l\rvert, v, \gamma) . \tag{88}$$

Here and in the subsequent discussion, the choice of phase is represented by 0 or π instead of the general form of (85). The possible combinations of the phases ϱ and δ are summarized in Table 5 with the symmetry (parity) of the linear combinations in (83), where E^+, E^-, O^+, and O^- notations are used in analogy with the asymmetric top wavefunction by using the correspondence between K and $\lvert l\rvert$.

Equation (86) requires the "arbitrary" phases in (60) and (61) be related by $\delta = \xi - \eta = n\pi$. In most published discussions the phase choices are not given explicitly by these two equations, but implicitly by fixing the matrix elements of $q^{\pm}$ and $\hat{p}^{\pm}$. Typical choices of ξ and η are summarized in Table 6 with the various resulting matrix elements.

VIII. *l*-Type Doubling

The *l*-type doubling of a linear molecule is caused by the perturbation term [19, 20]

$$\begin{aligned} \hat{H}' = &- {}^{[\varrho\varrho]}Z^{[tt]} \{(\hat{p}^+)^2 (\hat{J}_{\mathrm{r}}^-)^2 + (\hat{p}^-)^2 (\hat{J}_{\mathrm{r}}^+)^2\}/\hbar^4 \\ &- {}^{[\varrho\varrho]}Z_{[tt]} \{(q^+)^2 (\hat{J}_{\mathrm{r}}^-)^2 + (q^-)^2 (\hat{J}_{\mathrm{r}}^+)^2\}/\hbar^2 , \end{aligned} \tag{89}$$

where we consider only one bending vibration. The matrix elements of the above operator can be calculated to be

$$\begin{aligned} \langle J, l \pm 2, v \rvert \hat{H}' \lvert J, l, v\rangle &= (q/4) \exp[\mp 2 i \varrho] \exp[\pm i \delta] \\ &\quad \cdot \{[J(J+1) - l(l \pm 1)][J(J+1) \\ &\quad - (l \pm 1)(l \pm 2)](v \pm l + 2)(v \mp l)\}^{1/2} , \end{aligned} \tag{90}$$

Table 5. Symmetry of the Wang-type linear combinations for linear molecule wavefunctions for E^* operation[a].

Phase $2\varrho - \delta$		l	γ	even J	odd J	e or f[b]
0	E^+	e	e	+	−	e
	E^-	e	o	−	+	f
	O^+	o	e	−	+	f
	O^-	o	o	+	−	e
π	E^+	e	e	+	−	e
	E^-	e	o	−	+	f
	O^+	o	e	+	−	e
	O^-	o	o	−	+	f

[a] Symmetry for E^* is usually called parity, and indicated by + (symmetric) and − (antisymmetric).
[b] See Ref. [25].

Table 6. Matrix elements of $q^{\pm}$ and $\hat{p}^{\pm}$ in various choices of phases[a].

	Phase choices							
	(i) $\delta=\xi-\eta=0$				(ii) $\delta=\xi-\eta=\pi$			
	$\xi=0$	$\pi/2$	π	$3\pi/2$	0	$\pi/2$	π	$3\pi/2$
	$\eta=0$	$\pi/2$	π	$3\pi/2$	π	$3\pi/2$	0	$\pi/2$
$\langle v+1, l+1 \| \hat{p}^+/\hbar \| v, l\rangle$	f	if	$-f$	$-if$	f	if	$-f$	$-if$
$\langle v+1, l+1 \| q^+ \| v, l\rangle$	$-if$	f	if	$-f$	$-if$	f	if	$-f$
$\langle v-1, l+1 \| \hat{p}^+/\hbar \| v, l\rangle$	g'	$-ig'$	$-g'$	ig'	$-g'$	ig'	g'	$-ig'$
$\langle v-1, l+1 \| q^+ \| v, l\rangle$	ig'	g'.	$-ig'$	$-g'$	$-ig'$	$-g'$	ig'	g'
$\langle v+1, l-1 \| \hat{p}^-/\hbar \| v, l\rangle$	f'	if'	$-f'$	$-if'$	$-f'$	$-if'$	f'	if'
$\langle v+1, l-1 \| q^- \| v, l\rangle$	$-if'$	f'	if'	$-f'$	if'	$-f'$	$-if'$	f'
$\langle v-1, l-1 \| \hat{p}^-/\hbar \| v, l\rangle$	g	$-ig$	$-g$	ig	g	$-ig$	$-g$	ig
$\langle v-1, l-1 \| q^- \| v, l\rangle$	ig	g	$-ig$	$-g$	ig	g	$-ig$	$-g$

[a] $f=[(v+l+2)/2]^{1/2}$, $f'=[(v-l+2)/2]^{1/2}$, $g=[(v+l)/2]^{1/2}$, and $g'=[(v-l)/2]^{1/2}$.

where the arbitrary phases are explicitly included. The quantity q is called the l-type doubling constant:

$$q=-2\left\{{}^{[\varrho\varrho]}Z^{[tt]}+{}^{[\varrho\varrho]}Z_{[tt]}\right\} \tag{91}$$

which in the harmonic approximation is

$$q=(2B^2/\omega_t)\cdot\left[1+4\sum_s(\zeta^x_{ts})^2\omega_t^2/(\omega_s^2-\omega_t^2)\right]. \tag{92}$$

This quantity q is independent of the phase choice. The problem is that what is used by most spectroscopists is not this q but the value including the arbitrary phase factor,

$$\tilde{q}=q\exp[\mp i(2\varrho-\delta)]. \tag{93}$$

The first order energy correction due to the l-type doubling interaction in the $|l|=1$ state can be calculated by the matrix elements of the perturbation Hamiltonian $\hat{H}'$ using the Wang-type linear combination in (83) to be

$$(J,1,v,\gamma\,|\,\hat{H}'\,|\,J,1,v,\gamma)=(-1)^{\gamma}\cos(2\varrho-\delta)(q/4)(v+1)J(J+1). \tag{94}$$

The problem is exactly the same as that given in Sect. V for the K-type doubling of an asymmetric rotor. Equation (94) should be compared with the last term in (39). The energy correction given in (94) changes its sign when the phase $(2\varrho-\delta)$ is changed. In the case of K-type doubling, the parameter $(B-C)$ is always positive by definition. However, in the case of l-type doubling the parameter q can conceivably be positive or negative. Therefore there are four possible cases of correspondences between the energy levels and wavefunctions as summarized in Table 7. The important result is that if q is positive, the upper l-type doubling component for $|l|=1$ is of symmetry f for any choice of phase and the lower is of e, and this relation is reversed when q is

Table 7. Correspondence between wavefunctions and energy levels in l-type doubling components of a linear molecule in $|l|=1$ state.

			Phase choice			
			(i) $2\varrho-\delta=0$		(ii) $2\varrho-\delta=\pi$	
q	l-doubling	symmetry	$\tilde{q}$	w.f.	$\tilde{q}$	w.f.
positive	upper lower	f e	>0	O^+ O^-	<0	O^- O^+
negative	upper lower	e f	<0	O^- O^+	>0	O^+ O^-

negative. However we have to be careful about the fact that the value of the l-type doubling constant given in most papers is not q but $\tilde{q}$ which includes the phase contribution. The sign of $\tilde{q}$ is also listed in Table 7 in order to make this point clear.

IX. l-Type Doubling in Symmetric-Top Molecules

For completeness we discuss in this section the symmetry properties of the rovibrational wavefunctions and l-type doubling of a symmetric-top molecule. Since the most common symmetry of the symmetric top molecules is C_{3v}, we discuss here only molecules of this symmetry, e.g., CH_3X, of which the character table is listed in Table 8. The wavefunctions are given by (78). For simplicity we consider one degenerate vibration only;

$$\psi = |J, k, m\rangle |v, l\rangle = |J, k, v, l\rangle . \qquad (95)$$

The rotational part of the wavefunction has the symmetry properties given in (30). Thus, using the equivalent rotations of the symmetry operations, the following transformations are obtained:

$$(123)\,|J, k, m\rangle = \exp[2\pi i k/3]\,|J, k, m\rangle$$

and

$$(23)^*\,|J, k, m\rangle = (-1)^{J+k} \exp[2 i \varrho k]\,|J, -k, m\rangle . \qquad (96)$$

The vibrational part of the wavefunction is the THO wavefunction discussed in Section VI. By rotating the molecule-fixed axis about the z axis by β (R_z^β operation) the angle coordinate of the degenerate vibration α is transformed as

$$\alpha \rightarrow \alpha - \beta . \qquad (97)$$

By a simple geometrical consideration it is concluded that the operators $q^\pm$ and $\hat{p}^\pm$ are transformed by R_z^β as

$$q^\pm \rightarrow \exp[\mp i \beta] q^\pm$$

and

$$\hat{p}^\pm \rightarrow \exp[\mp i \beta] \hat{p}^\pm . \qquad (98)$$

Table 8. Molecular symmetry group C_{3v}.

C_{3v} equiv. rot.	E R^0	(123) $R_z^{2\pi/3}$	$(23)^*$ R_y^π
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0

From these transformation properties, (97) and (98), the following operator equation can be proved:

$$R_z^\beta \hat{R}^{\pm(\pm)} = \exp[(\mp) i \beta] \hat{R}^{\pm(\pm)} R_z^\beta . \qquad (99)$$

A similar method used in (75) can be applied to obtain the transformation property of the function $|v, l\rangle$,

$$R_z^\beta |v, l\rangle = \exp[-i \beta l]\,|v, l\rangle . \qquad (100)$$

Since the equivalent rotation of the (123) operation is $R_z^{2\pi/3}$, and since the radial variable of the degenerate vibration is invariant under the symmetry operation, we can conclude that the function $|v, l\rangle$ is transformed by the (123) operation as

$$(123)\,|v, l\rangle = \exp[-2\pi i l/3]\,|v, l\rangle . \qquad (101)$$

The equivalent rotation of the (23)* operation is R_y^π, which is the same as that of E^* in a linear molecule. Therefore the function $|v, l\rangle$ should be transformed by (23)* in a similar way as given in (77)

$$(23)^*\,|v, l\rangle = \exp[-i \delta l]\,|v, -l\rangle . \qquad (102)$$

Combining (96), (101), and (102), the symmetry properties of the rovibrational wavefunctions of a symmetric-top molecule is obtained as

$$(123)\,|J, k, v, l\rangle = \exp[-2\pi i (l - k)/3]\,|J, k, v, l\rangle ,$$

and

$$(23)^*\,|J, k, v, l\rangle = (-1)^{J+k} \exp[i(2\varrho k - \delta l)]\,|J, -k, v, -l\rangle . \qquad (103)$$

These symmetry properties should be compared with those expressed in a traditional method, e.g., by Oka [21], where the phase factor is not explicitly given.

The symmetry species A or E is distinguished by the transformation property under the (123) operation. As can be seen in the upper equation of (103), the character for this operation is determined by the number $(l - k)$, which is Hougen's quantum number G [22]. When $|G| = |l - k| = 3n$, $n =$ integer, the function $|J, k, v, l\rangle$ is of symmetry A, and when $|G| \neq 3n$, the pair of functions, $|J, k, v, l\rangle$ and $|J, -k, v, -l\rangle$ belongs to the E species. In this distinction between the A and E species, the phase factor plays no role. The A_1 and A_2 symmetry, however, are distinguished by the second equation of (103) which includes the phases of the rotational and vibrational wavefunctions.

If the phases of the wavefunctions are properly chosen

$$2\varrho k - \delta l = 0 \quad \text{or} \quad \pi\,, \tag{104}$$

the Wang-type linear combinations of the pair functions

$$|J, K, v, l, \gamma) = \{|J, K, v, l\rangle + (-1)^{\gamma}|J, -K, v, -l\rangle\}/\sqrt{2}\,, \tag{105}$$

form a basis set of the irreducible representation; A_1 and A_2 for $|G| = 3n$ and E for $|G| \neq 3n$. In the above equation, $K = |k|$ as usual, but l is still a signed quantity in both sides. It is assumed in (105) that at least k or l is not zero. If both k and l are nonzero, then there are four states for a given K and $|l|$, which are degenerate in zero-th order approximation: two wavefunctions of $|J, K, v, |l|, \gamma)$ and two of $|J, K, v, -|l|, \gamma)$. Now we discuss only the special case of $K = 1$ and $|l| = 1$, which is most important. In this case, the functions $|J, K, v, |l|, \gamma)$ are linear combinations of functions with $G = 0$, and the functions $|J, K, v, -|l|, \gamma)$ are linear combinations of $|G| = 2$ functions. Therefore the former functions are of A_1 and A_2 species, and the latter are of E species. In the language of spectroscopy, we say that the A and E states are separated by the first order Coriolis interaction. The degenerate E state cannot be separated any more. The two A states are separated into A_1 and A_2 states by the *l*-type doubling. Since the A_1 and A_2 functions of the $K = |l| = 1$ state are combinations of $k = l$ wavefunctions, they are exactly the same as those of a linear molecule given in (83). Therefore the symmetry properties and the correspondences between the energy levels and wavefunctions in the *l*-type doubling components are exactly the same as those discussed in Sect. VII and VIII for linear molecules.

However, very unfortunately, the phases of the rovibrational wavefunctions for a symmetric top are often chosen by spectroscopists differently from those of the linear molecule. This discrepancy seems to originate in the history of vibration-rotation theory.

X. Comments

Sometimes the ladder operators of the molecule-fixed angular momentum are defined by

$$\hat{J}^{\pm}_{r1} = \hat{J}_y \pm i\hat{J}_x\,, \tag{106}$$

e.g., Nakagawa and Morino [19] and Oka [21], instead of by (13). This operator can be related to our ladder operator by

$$\hat{J}^{\pm}_{r1} = \pm\, i\hat{J}^{\pm}_{r}\,. \tag{107}$$

Therefore if we change the definition of the ladder operator as in (106), we will see the phase of the wavefunction shift by $\pi/2$.

A similar phase shift occurs if we use the I^l axis representation [15] in the asymmetric top Hamiltonian. The ladder operator in the I^r representation which is used in the present work is

$$\hat{J}^{\pm}_{r} = \hat{J}_b \pm i\hat{J}_c\,, \tag{108}$$

and in the I^l representation is

$$\hat{J}^{\pm}_{r2} = \hat{J}_c \pm i\hat{J}_b\,. \tag{109}$$

The difference between the definitions (108) and (109) is exactly the same as that between (13) and (106). Thus this change of definition also results in a phase shift of $\pi/2$.

Such a freedom to define the angular momentum ladder operators also exists in the definition of the ladder operators for the two-dimensional isotropic harmonic oscillator. We have to be careful about which definition of the ladder operators is used, which molecule-fixed axis representation is used, and which phase factor is used in the ladder operator matrix elements.

Cartwright and Mills [23] introduced an additional sign factor for the *l*-type doubling phenomenon which is operationally defined: the sign factor is so chosen that the sign obtained for $\tilde{q}$ agrees with the conventionally defined one. However, as we have seen, the sign of the phase-independent q can be obtained if the symmetry of the *l*-doubling component is known. It is in principle possible to identify the symmetry of the level by combining microwave spectra and high resolution infrared spectra. The former can provide exact information on the effective B constants for the doublets, from which we can distinguish the upper and lower component of the doublets. On the other hand, the latter gives symmetry information from the selection rule.

Blass [24] discussed similar problems arising from the phase choices in the case of first order Coriolis resonances in C_{3v} molecules. The present discussion can be applied to this problem also.

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