Symmetry Properties of Rovibronic States of an X_3 Molecule in an Upright Conical Potential

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The rovibronic structure of cone states of an X_3 type molecule is investigated to provide a detailed understanding of the effect of the geometrical phase. When compared to the rovibronic structure of a system in which no geometrical effect is present, a dramatic duplication of the number of rotational levels ($k \neq 0$) is observed for certain vibrational states ($\ell = 0$) including the vibrational ground state. Rotational structure may serve as a diagnostic tool to detect the presence of a conical intersection.

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Introduction.—As shown by Jahn and Teller [1], a symmetric nonlinear nuclear configuration of a molecule in a degenerate electronic state is unstable. In the case of a molecule in an E electronic state, distortion of the symmetric configuration leads to a splitting of the electronic potential energy surface into two sheets. There is a conical intersection of the two sheets at the symmetric configurations. Since Longuet-Higgins *et al.* [2,3] have demonstrated that the two adiabatic electronic wave functions, which form the degenerate state, change sign when transported adiabatically on a closed loop around the conical intersection, there exists a vast literature on the effect of the geometrical phase; see [4] and references therein, in particular, on the rovibrational states on the lower sheet of the split potential energy surface. As far as the upper sheet is concerned, to the best of our knowledge the only reported results of a rovibronic calculation are those on H_3 due to Lepetit *et al.* [5]. Such cone states are of course coupled to the lower sheet of the potential energy surface and thus they are resonance states. However, they are expected to be quite stable, as shown originally by Slonczewski [6]. It is the purpose of the present Letter to explore in detail the rovibrational structure of the cone states. Following the definition of appropriate spectroscopic quantum numbers, we will establish a correlation between rovibronic states with and without geometrical phase to understand the effect of such a phase.

Vibronic cone states and their symmetry properties.—The natural basis for a symmetry classification of the vibronic cone states is the three-particle permutation inversion group, $S_3 \times I$. The states can be labeled according to the angular momentum quantum number J, their irreducible representation, and the corresponding counting index as (J, Γ, i). The permutation inversion symmetry can be exploited easily in hyperspherical coordinates, so that the most efficient methods for the calculation of the rovibronic states are those based on such coordinates. Though the symmetry classification of the calculated states within $S_3 \times I$ is exact, it does not lead to an understanding of the rovibronic structure, and it is desirable to have in addition a classification in terms of less rigorous spectroscopic quantum numbers. Watson [7] has studied in detail the rovibrational structure of an X_3 type molecule and has devised a set of rotational quantum numbers that hold if there is no geometrical effect (NGP case). If such an effect is present (GP case), his quantum numbers need to be revised. To obtain appropriate quantum numbers, consider the effect of the operators of $S_3 \times I$ on a conventional rovibronic basis,

$$|v_1 v_2 \ell J k \alpha\rangle = |v_1 v_2 \ell\rangle |Jk\rangle e^{i\alpha\phi}. \tag{1}$$

Here, v_1 and v_2 denote the quantum numbers of the symmetric stretch and the degenerate bending vibration, respectively, and ℓ the vibrational angular momentum which takes the values $\ell = v_2, v_2 - 2, \ldots - v_2$. J is the total angular momentum and k its internal projection. The electronic spin will not be considered here. $e^{i\alpha\phi}$ is a phase factor, where ϕ is the phase angle and α, in general, is a function in configuration space [8]. In its most basic form, it may be chosen as a constant, taking the values zero (NGP) or $\frac{1}{2}$ (GP) such as to satisfy the cycling boundary conditions. The symmetry operators of $S_3 \times I$ affect the phase angle ϕ and the three Euler angles. Following Longuet-Higgins *et al.* [2,3], Hougen [9,10], and Watson [7] we obtain for the cyclic permutation operator (123)

$$(123)|v_1 v_2 \ell\rangle = e^{-(2\pi i/3)\ell} |v_1 v_2 \ell\rangle \tag{2}$$

and

$$(123)|Jk\rangle = e^{(2\pi i/3)k} |Jk\rangle. \tag{3}$$

In the above equations, we have observed the phase convention in the ϕ angle due to Longuet-Higgins *et al.* [2,3]. The effect of (123) on the combined functions of Eq. (1) is thus

$$(123)|v_1 v_2 \ell J k \alpha\rangle = e^{(2\pi i/3)(k-\ell-\alpha)} |v_1 v_2 \ell J k \alpha\rangle. \tag{4}$$

Permutation of particles 2 and 3 has the effect

$$\begin{aligned}(23)|v_1 v_2 \ell J k \alpha\rangle &= (-1)^{J-k} |J, -k\rangle e^{i\pi\ell} |v_1 v_2, -\ell\rangle e^{i\alpha(\pi-\phi)} \\ &= (-1)^J e^{-i\pi(k-\ell-\alpha)} |v_1 v_2, -\ell, J, -k, -\alpha\rangle.\end{aligned} \tag{5}$$

TABLE I. Symmetry classification of the spectroscopic functions, Eq. (11). Integer values of G correspond to the NGP case, half integer values of G to the GP case.

	$(-1)^k = 1$	$(-1)^k = -1$
$G = 0, 3, \ldots$	A_1'/A_2'	A_1''/A_2''
$G = 1, 4, \ldots$	E'	E''
$G = 2, 5, \ldots$	E'	E''
$G = \frac{3}{2}, \frac{9}{2}, \ldots$	A_1'/A_2'	A_1''/A_2''
$G = \frac{1}{2}, \frac{7}{2}, \ldots$	E'	E''
$G = \frac{5}{2}, \frac{11}{2}, \ldots$	E'	E''

Inversion of the coordinate system leaves the internal coordinates unchanged, but affects the Euler angles [11] and results in

$$E^\star|v_1v_2\ell Jk\alpha\rangle = (-1)^k|v_1v_2\ell Jk\alpha\rangle. \tag{6}$$

Since the parity is completely determined by k and since the permutation operators conserve $|k|$, we can construct the symmetrized functions by using the projection operators of just the permutation group, S_3. The effect of the remaining permutation operators, $(123)^2$, 12, and 13 can be obtained in a straightforward manner from the above equations and the relations

$$(12) = (123)(23)(123)^2, \qquad (13) = (123)^2(23)(123). \tag{7}$$

Finally, acting the projection operators of the irreducible representations of S_3 on the basis Eq. (1) yields

$$P_{A_1/A_2}|v_1v_2\ell Jk\alpha\rangle = (1+a)|v_1v_2\ell Jk\alpha\rangle \pm (-1)^J b|v_1v_2, -\ell, J, -k, -\alpha\rangle, \tag{8}$$

where the plus sign refers to A_1 and the minus sign to A_2, and

$$P_E|v_1v_2\ell Jk\alpha\rangle = (2-a)|v_1v_2\ell Jk\alpha\rangle, \tag{9}$$

with the coefficients a and b obtained as $a = e^{(2\pi i/3)(k-\ell-\alpha)} + e^{(4\pi i/3)(k-\ell-\alpha)}$ and $b = e^{\pi i(k-\ell-\alpha)}(1 + e^{(2\pi i/3)(2k-2\ell-2\alpha)} + e^{(2\pi i/3)(-2k+2\ell+2\alpha)})$. In the case of the geometrical phase effect, the coefficient b in Eq. (8) has to be replaced by ib, since we have to use the characters of the double valued representations (A_1/A_2 correspond to the double group representations $E^+_{3/2}/E^-_{3/2}$; see Ref. [10]). The two coefficients depend on $g = k - \ell - \alpha$, which, in view of Eq. (8), leads to the definition of

$$G = |k - \ell - \alpha|, \tag{10}$$

a quantity that will be discussed below. The numerical values of the coefficients are found to be [$a = 2, b$ (or ib) $= 3$] for $G = 0, \frac{3}{2}$(mod3) and ($a = -1, b = 0$) for $G = \frac{1}{2}, 1, 2, \frac{5}{2}$(mod3), so that we obtain the desired symmetrized spectroscopic functions as

$$|v_1v_2GJ\rangle_\pm = \frac{1}{\sqrt{2}}[|v_1v_2, \ell+\alpha\rangle|Jk\rangle \pm (-1)^J|v_1v_2, -\ell-\alpha\rangle|J, -k\rangle] \tag{11}$$

$$= \frac{1}{\sqrt{2}}[|v_1v_2\ell\rangle|Jk\rangle \pm (-1)^J|v_1v_2, -\ell-2\alpha\rangle|J, -k\rangle]e^{i\alpha\phi}. \tag{12}$$

TABLE II. NGP rovibronic term values, in eV, of the lowest states $(v_1, v_2^{|\ell|})$ with $\ell = 0$.

J	G	s	Γ	$(0, 0^0)$	$(1, 0^0)$	$(2, 0^0)$	$(3, 0^0)$
0	0	+1	A_1'	3.7210	3.9216	4.1067	4.2759
1	1		E''	3.7264	3.9266	4.1114	4.2802
1	0	+1	A_2'	3.7294	3.9284	4.1130	4.2817

TABLE III. NGP rovibronic term values, in eV, of the lowest states $(v_1, v_2^{|\ell|})$ with $\ell = 1$.

J	G	s	Γ	$(0, 1^1)$	$(1, 1^1)$	$(2, 1^1)$	$(3, 1^1)$
0	1		E'	4.2886	4.4533	4.5980	4.7212
1	2		E''	4.2904	4.4550	4.5996	4.7275
1	1		E'	4.2955	4.4596	4.6036	4.7261
1	0	+1	A_2''	4.2969	4.4608	4.6047	4.7270
1	0	−1	A_1''	4.2971	4.4610	4.6049	4.7272

In Eq. (12), the geometrical phase factor $e^{i\alpha\phi}$ has been extracted from the basis kets to obtain an expression similar to that given in Ref. [12]. The symmetry properties of the above functions are collected in Table I.

We will now turn our attention to the quantity G defined above. Since G is only defined modulo 3, an extended G cannot serve as a rigorous quantum number. However, it is useful as a "good" quantum number, and the functions of Eq. (11) have been constructed to define the spectroscopic quantum numbers needed in a classification of the exact "hyperspherical" states. The appearance of the difference $k - \ell$ in the definition of G might

TABLE IV. GP rovibronic term values, in eV, of the lowest states $(v_1, v_2^{|\ell|+1/2})$ with $\ell = 0$ $(j = \frac{1}{2})$.

J	G	U	s	Γ	$(0, 0^{1/2})$	$(1, 0^{1/2})$	$(2, 0^{1/2})$	$(3, 0^{1/2})$
0	$\frac{1}{2}$			E'	4.0215	4.2049	4.3710	4.5189
1	$\frac{3}{2}$		+1	A_2''	4.0243	4.2076	4.3734	4.5210
1	$\frac{3}{2}$		−1	A_1''	4.0256	4.2087	4.3744	4.5220
1	$\frac{1}{2}$	+1		E''	4.0284	4.2113	4.3768	4.5241
1	$\frac{1}{2}$	−1		E'	4.0286	4.2114	4.3769	4.5243

TABLE V. GP rovibronic term values, in *eV*, of the lowest states $(v_1, v_2^{|\ell|+1/2})$ with $\ell = 1$ $(j = \frac{3}{2})$.

J	G	s	Γ	$(0, 1^{3/2})$	$(1, 1^{3/2})$
0	$\frac{3}{2}$	$+1$	A_1'	4.5005	4.6425
0	$\frac{3}{2}$	-1	A_2'	4.5700	4.7177
1	$\frac{5}{2}$		E''	4.5050	4.6466
1	$\frac{3}{2}$	$+1$	A_2'	4.5071	4.6484
1	$\frac{3}{2}$	-1	A_1'	4.5768	4.7237
1	$\frac{1}{2}$		E''	4.5733	4.7223

appear arbitrary, since it is due to different phase conventions for the internal angle ϕ and the Euler angle α. If we had used identical phase conventions for the two angles, we would have arrived at the expression $G = |k + \ell + \alpha|$, which is equivalent to the definition Eq. (10) because k and ℓ are signed quantities. Thus, there is no ambiguity. For the treatment of GP states, where $\alpha = \frac{1}{2}$, it is useful to introduce the angular momentum j as

$$|j| = |\ell| + \alpha \tag{13}$$

and to reexpress G as

$$G = |k - \ell - \alpha| = |k - j|. \tag{14}$$

The good quantum number G as defined here is a generalization of Watson's quantum number, since it takes into account the effect of the geometrical phase. Even though this generalization may seem straightforward and standard methods of group theory were used to arrive at Eqs. (11) and (14), we have presented the derivations in some detail to demonstrate clearly the origin of the G quantum number. This is important since, to the best of our knowledge, the generalized G quantum number has never been used to classify GP states and since there are some peculiarities which do not occur in a NGP classification.

A case study.—To illustrate the use of the G quantum number, we have analyzed the resonance states in the upper conical potential of H_3. The positions of these states have been calculated by Lepetit *et al.* [5] with a hyperspherical method, and the states were assigned in terms of v_1, v_2, j, J, and Γ. Based on their observation that the GP effect produces a shift of about $\frac{1}{2}\hbar\omega_2$, the authors also presented an ordering scheme relating NGP and GP vibrational states. To gain additional insight, we have now rearranged most of their data and display them in separate tables according to the families $(v_1, v_2 = 0, \ell = 0)$, $(v_1, v_2 = 1, \ell = 1)$ or $(v_1, v_2 = 0, j = \frac{1}{2})$,

TABLE VI. Relation between the G quantum numbers in the NGP and GP cases.

$G_{\mathrm{NGP}} = \lvert k - \ell \rvert$		$G_{\mathrm{GP}} = \lvert k - j \rvert$	Relation
$G^+ = \lvert k \rvert + \lvert \ell \rvert$		$= \lvert k \rvert + \lvert j \rvert$	$G_{\mathrm{GP}}^+ = G_{\mathrm{NGP}}^+ + \frac{1}{2}$
$G^- =$ if $k > \ell$	$\lvert k \rvert - \lvert \ell \rvert$	$= \lvert k \rvert - \lvert j \rvert$	$G_{\mathrm{GP}}^- = G_{\mathrm{NGP}}^- - \frac{1}{2}$
if $k \le \ell$	$\lvert \ell \rvert - \lvert k \rvert$	$\lvert j \rvert - \lvert k \rvert$	$G_{\mathrm{GP}}^- = G_{\mathrm{NGP}}^- + \frac{1}{2}$

TABLE VII. NGP/GP correlation between the $\ell = 0$ rovibronic states. For the one-dimensional representations Γ_1/Γ_2, which are distinguished by $s = \pm 1$, the plus sign refers to Γ_1 and the minus sign to Γ_2.

J	G	U	s	Γ	$\lvert k \rvert$	G	U	s	Γ
0	0		$+1$	A_1'	0	$\frac{1}{2}$			E'
1	1			E''	1	$\frac{3}{2}$		± 1	A_2''/A_1''
					1	$\frac{1}{2}$	$+1$		E''
	0		$+1$	A_2'	0	$\frac{1}{2}$	-1		E'
2	2			E'	2	$\frac{5}{2}$			E'
					2	$\frac{3}{2}$	$+1$	± 1	A_1'/A_2'
	1			E''	1	$\frac{3}{2}$	-1	± 1	A_1''/A_2''
					1	$\frac{1}{2}$	$+1$		E''
	0		$+1$	A_1'	0	$\frac{1}{2}$	-1		E'
3	3		± 1	A_2''/A_1''	3	$\frac{7}{2}$			E''
					3	$\frac{5}{2}$	$+1$		E''
	2			E'	2	$\frac{5}{2}$	-1		E'
					2	$\frac{3}{2}$	$+1$	± 1	A_2'/A_1'
	1			E''	1	$\frac{3}{2}$	-1	± 1	A_2''/A_1''
					1	$\frac{1}{2}$	$+1$		E''
	0		$+1$	A_2'	0	$\frac{1}{2}$	-1		E'

TABLE VIII. NGP/GP correlation between the $\ell = 1$ rovibronic states.

J	G	U	s	Γ	$\lvert k \rvert$	G	U	s	Γ
0	1			E'	0	$\frac{3}{2}$		± 1	A_1''/A_2''
1	2			E''	1	$\frac{5}{2}$			E''
	1			E'	0	$\frac{3}{2}$		± 1	A_2'/A_1'
	0		± 1	A_2''/A_1''	1	$\frac{1}{2}$			E''
2	3		± 1	A_1'/A_2'	2	$\frac{7}{2}$			E'
	2			E''	1	$\frac{5}{2}$			E''
	1	$+1$		E'	0	$\frac{3}{2}$		± 1	A_1'/A_2'
	1	-1		E'	2	$\frac{1}{2}$	$+1$		E'
	0		± 1	A_1''/A_2''	1	$\frac{1}{2}$	-1		E''
3	4			E''	3	$\frac{9}{2}$		± 1	A_2''/A_1''
	3		± 1	A_2'/A_1'	2	$\frac{7}{2}$			E'
	2	$+1$		E''	1	$\frac{5}{2}$			E''
	2	-1		E''	3	$\frac{3}{2}$	$+1$	± 1	A_2''/A_1''
	1	$+1$		E'	0	$\frac{3}{2}$	-1	± 1	A_2'/A_1'
	1	-1		E'	2	$\frac{1}{2}$	$+1$		E'
	0		± 1	A_2''/A_1''	1	$\frac{1}{2}$	-1		E''

TABLE IX. NGP/GP correlation between the $\ell = 2$ rovibronic states.

J	G	U	s	Γ	$\|k\|$	G	U	s	Γ
0	2			E'	0	$\frac{5}{2}$			E'
1	3			A_2''/A_1''	1	$\frac{7}{2}$			E''
	2			E'	0	$\frac{5}{2}$			E'
	1			E''	1	$\frac{3}{2}$		± 1	A_2''/A_1''
2	4			E'	2	$\frac{9}{2}$		± 1	A_1'/A_2'
	3			A_1''/A_2''	1	$\frac{7}{2}$			E''
	2			E'	0	$\frac{5}{2}$			E'
	1			E''	1	$\frac{3}{2}$		± 1	A_1''/A_2''
	0			A_1'/A_2'	2	$\frac{1}{2}$			E'
3	5			E''	3	$\frac{11}{2}$			E''
	4			E'	2	$\frac{9}{2}$		± 1	A_2'/A_1'
	3			A_2''/A_1''	1	$\frac{7}{2}$			E''
	2			E'	0	$\frac{5}{2}$			E'
	1	$+1$		E''	1	$\frac{3}{2}$		± 1	A_2''/A_1''
	1	-1		E''	3	$\frac{1}{2}$	$+1$		E''
	0			A_2'/A_1'	2	$\frac{1}{2}$	-1		E'

$(v_1, v_2 = 1, j = \frac{3}{2})$ to which they belong, Tables II, III, IV, and V. Within these tables, the rovibronic states are assigned in terms of J and Watson's [7] quantum numbers G, U, and s. The s quantum number was introduced to distinguish between the two nondegenerate states with $G(\mathrm{mod}3) = 3$. It corresponds to the positive or negative Wang-type linear combinations in Eq. (11) and takes the values $s = \pm(-1)^J$. For $\ell = k = 0$, only $s = 1$ exists. The quantum number G itself is not unique, since states derived from $g = k - j$ and $g = k' + j$ with $k' = k - 2j$ lead to the same value of G. Such states can be distinguished by the quantum number U which takes the values $U = \pm 1$. Note that in the NGP case, the $U = \pm 1$ states have the same parity, whereas in the GP case they have different parity as here $(-1)^k \neq (-1)^{k-2j}$.

Turning our attention now again to Tables II, III, IV, and V, we notice that for a given value of J, the rotational energy generally increases with decreasing G, which makes G a useful quantum number. Indeed, the appearance in Table IV of two $J = 1$ states very close in energy, those of symmetry E'' and E', can be explained as due to the fact that they have the same value of G. Note that the states with A_1' or A_1'' symmetry are unphysical since they violate the Pauli principle, but are included in the tables for the sake of completeness. The geometrical phase considerably complicates the rotational structure of the $\ell = 0$ states; see Tables II and IV. To understand this, consider the relation between the quantum numbers G_{NGP} and G_{GP} as shown in Table VI. In general, forming all possible combinations $g = k - \ell$ of the signed quantities k and ℓ yields two values of G for each set of (k, ℓ). The analysis presented in Table VI shows that each NGP state has a GP counterpart, except for the case $\ell = 0$. Here we find the relations $(G_{\mathrm{NGP}} = 0 \Leftrightarrow G_{\mathrm{GP}} = \frac{1}{2})$ and $(G_{\mathrm{NGP}} = |k| \neq 0 \Leftrightarrow G_{\mathrm{GP}} = G_{\mathrm{NGP}} \pm \frac{1}{2})$. A correlation between the NGP and GP rotational states can now be found by ordering each set of states with respect to G and relating them through their common values of $|k|$. Explicit results are presented in Tables VII, VIII, and IX for $\ell = 0, 1, 2$ and $J \leq 3$.

Conclusions.—It has been shown here that generalized Watson type quantum numbers account for the rovibronic structure of resonance states in a conical potential. Such an analysis does not only apply to H_3. There are other important triatomic systems which show a conical intersection, such as the alkali trimers (see [4] for references) which are isoelectronic with H_3, or $H_3{}^+$ in its excited electronic triplet state [13,14] and isoelectronic species, to which such a symmetry classification should be applied.

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