IV. APPLICATIONS TO NONRIGID MOLECULES

A. Introduction and the Unsymmetrical Bent XH_2 Molecule

A nonrigid molecule is a molecule that can contort (i.e., vibrate with a large amplitude) from one conformation to another in a time scale short enough to be experimentally detectable (i.e., observable energy-level splittings or shifts are produced). The ammonia and dimethylacetylene molecules are examples of molecules that can undergo very rapid contortions; the ammonia molecule inverts and the dimethylacetylene molecule twists. As a result of the contortional tunneling there are usually energy-level splittings, and the size of the MS group increases over that of one conformer. In this section we study the general principles behind the classification of the rovibrational states in the enlarged MS group and the determination of overall selection rules. It proves very useful to separate these selection rules into rotational, contortional, and vibrational parts; this is also discussed. In this section we use the molecules "unsymmetrical XH_2", ammonia, methanol, acetone, and dimethylacetylene as examples and in Sec. IV.F we briefly discuss B_2F_4, CH_3NO_2, ferrocene, CH_3SiH_3, $C(CH_3)_4$, $M(NH_3)_6$, cyclobutane, cyclopentane, $Y_4X\text{-}XY_4$, and H_2O_2. Dimethylacetylene is an example of a nonrigid molecule that has identical coaxial rotors on a linear framework, and to classify separately the rotational, contortional, and vibrational wavefunctions of such molecules it is necessary to use an extended molecular symmetry group (usually just the double group).

In view of the discussion given above of the symmetry properties of the energy levels of the water molecule, a very convenient example for demonstrating general principles will be provided by a hypothetical bent unsymmetric XH_2 molecule (i.e., the molecule is such that in the equilibrium configuration one HX bond is longer than the other). An excited electronic state of SO_2 probably provides an example of such a bent unsymmetric AB_2 molecule [24]. Labeling the H atoms 1 and 2 we see that this unsymmetrical molecule exists in two different numbered conformations: the left- and right-handed forms of Fig. 13. We further imagine that the potential surface in the direction of the antisymmetric stretching coordinate is as drawn in Fig. 14; the contortional tunneling splittings in the first four levels of the antisymmetric stretching vibration (i.e., $v_a = 0, 1, 2,$ and 3) are all less than 0.001 cm^{-1}.

One important point for nonrigid molecules concerns the definition of the molecule-fixed axes. For a rigid unsymmetrical XH_2 molecule in its equilibrium configuration we define the molecule-fixed axes to be the principal axes with "b" in the X-direction and "a" in the H_2 direction. When the molecule is not in its equilibrium configuration the axes are located by the three Eckart conditions [47]. For a nonrigid unsymmetrical XH_2 molecule the reference configuration is that in which only the unsymmetrical stretching coordinate does not have its equilibrium value and then the molecule-fixed axes may or may not be chosen as the principal axes (see pages 140-141 of [27]). For a nonrigid unsymmetrical XH_2 molecule not in its reference configuration the axes are located by the three Eckart conditions and the value of the unsymmetrical stretching coordinate is fixed by the Sayvetz condition. See Eqs. (7) and (8) of [27].

We will now again see how unfeasible elements of the CNPI group are useless from the point of view of making symmetry distinctions between energy levels. In the infrared or Raman spectrum of this XH_2 molecule we would not normally see levels with $v_a > 3$, and so no splittings due to tunneling would be resolved. The CNPI group of this molecule is the group [E, (12), E*, (12)*] (see Table A2) but following the prescription of Longuet-Higgins [1] the elements (12) and (12)* are unfeasible since they interchange the left- and right-handed conformations, which are separated by an insuperable energy barrier (no splittings seen in our infrared or Raman experiments). Thus the MS group $C_s(M)$ of

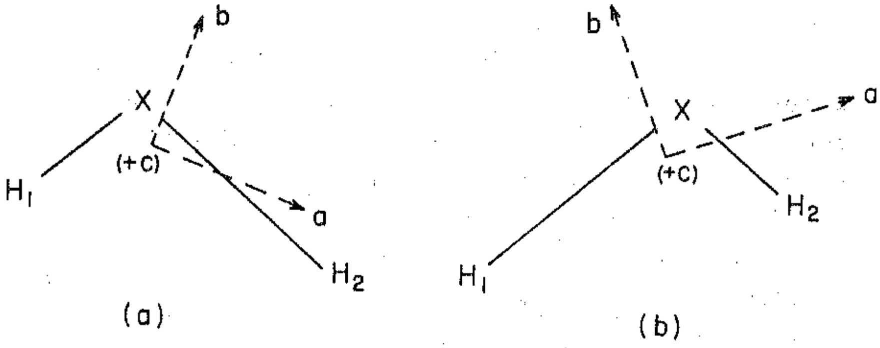

FIG. 13. The two numbered conformers of a hypothetically unsymmetric XH_2 molecule. The principal inertial axes of each conformer are labeled: (a) left-handed, (b) right-handed.

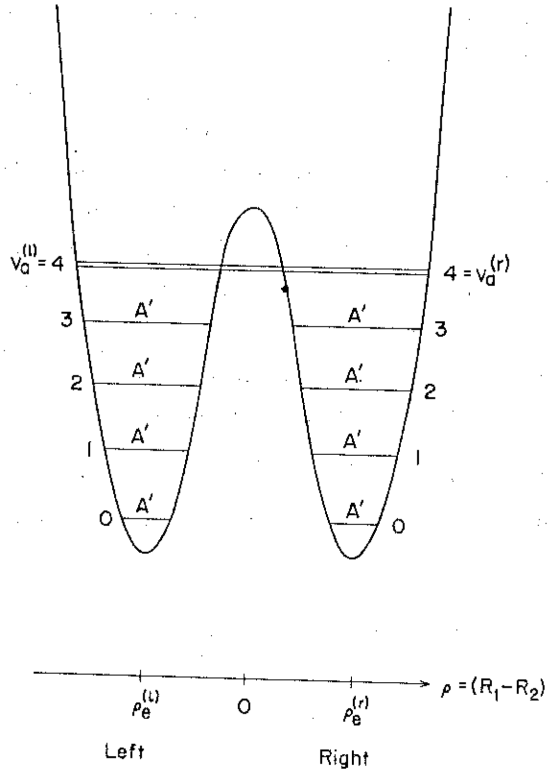

FIG. 14. The potential function of the unsymmetrical XH_2 molecule in the direction of the antisymmetric stretch. The $J = 0$ energy levels are also shown.

this molecule is [E, E*] with character table and C_s point-group isomorphism as shown in Table A5. All the observed rovibrational states can be classified as A' or A'' in the MS group following the procedures discussed in Sec. III for either the left- or right-handed molecule. All the vibrational wavefunctions are of species A' and the rotational wavefunctions for K_aK_c of ee or oe type are A', while those of oo or eo type are A''. All four nuclear-spin states are of A' symmetry and the overall wavefunction can be A' or A'', so that all levels have the same statistical weight of 4 and there will be no intensity alternations. States of the same symmetry in the MS group can perturb each other, and allowed dipole transitions occur between levels connected by the species A'' (with $\Delta J = 0, \pm 1$). Also the potential function determined from the vibrational energy levels would yield the result of Fig. 15.

We could also use the CNPI group to classify the levels since it is a symmetry group of the Hamiltonian. The operations (12) and (12)* both interchange R_1 and R_2, and thus send ρ to $-\rho$ (where $\rho = R_1 - R_2$); they each have the effect of interchanging rovibrational functions of the left- and right handed molecules. A particular rovibrational level $(v;\ J_{K_aK_c})$ of symmetry A', say, in the MS group is really doubly degenerate with one wavefunction of A' symmetry for the left-handed molecule $\psi_\ell(v;\ J_{K_aK_c})$, and one of A' symmetry for the right-handed molecule, $\psi_r(v;\ J_{K_aK_c})$; we have classified either ψ_ℓ or ψ_r in the preceding paragraph. We can write

$$(12)\psi_\ell^{A'}\ (v;\ J_{K_aK_c}) = \psi_r^{A'}\ (v;\ J_{K_aK_c})$$

and

$$(12)^*\psi_\ell^{A'}(v;\ J_{K_aK_c}) = \psi_r^{A'}(v;\ J_{K_aK_c}) \tag{37}$$

Thus this pair of functions transforms as $(A_1 + B_2)$ of the CNPI group of Table A2; $(\psi_r^{A'} + \psi_\ell^{A'})$ being A_1 and $(\psi_r^{A'} - \psi_\ell^{A'})$ being B_2.

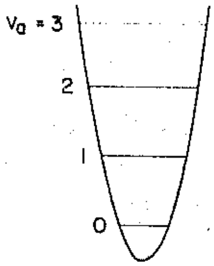

FIG. 15. The J = 0 energy levels and potential curve determined by studying the spectrum of the unsymmetric XH_2 molecule with $v_a \leq 3$.

Similarly the A" function correlates with the species $(A_2 + B_1)$ of the CNPI group; $(\psi_r^{A''} + \psi_\ell^{A''})$ being A_2 and $(\psi_r^{A''} - \psi_\ell^{A''})$ being B_1. We could classify all the wavefunctions in the CNPI group, but this would add nothing new in the way of allowing us (i) to distinguish between energy levels, (ii) to determine which levels can perturb each other, or (iii) to determine which levels are connected by allowed transitions or by electric or magnetic fields. Using the CNPI group would simply mean that everywhere we get A' from the MS group we would get $(A_1 + B_2)$, and A" would become $(A_2 + B_1)$. This is why the unfeasible operations (12) and (12)* are useless; in the event that tunneling splittings are not resolved no new useful information is obtained by including them in the group.

Let us suppose that we put this XH_2 into a hot long-path-length cell and that we can see the $v_a = 4$ level and resolve the tunneling splitting. To classify these split levels and the lower unsplit levels we would now need to use the CNPI group, C_{2v} (M), since both (12) and (12)* are feasible (some splitting has been resolved), and they provide useful symmetry distinctions. Once the splittings are resolved there are four symmetry types of energy level: viz., A_1, A_2, B_1, and B_2. A level of symmetry A'(A") having statistical weight 4 in the C_s(M) group splits into an $A_1(A_2)$ and a $B_2(B_1)$ level of the C_{2v}(M) group with statistical weights of 1 and 3, respectively. The vibrational states associated with the antisymmetric stretch split into A_1 and B_2 states of the tunneling molecule; those with an even number of nodes in the wavefunction $(\psi_r + \psi_\ell)$ will be A_1 (v_a of the symmetric XH_2 molecule would be even), and those with an odd number of nodes $(\psi_r - \psi_\ell)$ will be B_2 (v_a of the symmetric XH_2 molecule would be odd). Allowed electric-dipole transitions will occur between rovibrational states connected by the species A_2 with the restriction $\Delta J = 0, \pm 1$. The addition of the data about the $v_a = 4$ level to those of the v_a = 0-3 levels would enable the height of the barrier to be roughly determined, whereas data on v_a = 0-3 only give the potential curve of Fig. 15. The subject of correlating the species of a conformer before tunneling with that after tunneling has been discussed in detail by Watson [10].

In the unsymmetrical $S^{16}O_2$ molecule the fact that the ^{16}O nucleus follows Bose statistics has a very important consequence. In an unsymmetrical SO_2 molecule the rovibronic levels are A' and A", and tunneling through the barrier splits the levels according to

(38)

as already discussed. However, the overall wavefunction must be A_1 or A_2 [i.e., unchanged by (12)] and the oxygen nuclear-spin wavefunction is A_1. Thus all rovibronic levels of B_1 or B_2 symmetry have no allowed nuclear-spin partner, and they are forbidden. Thus although it would appear that each rovibronic level ought to be split into two by tunneling, only one of each of these pairs is allowed because of the rules of Bose statistics (only rovibronic states of species A_1 or A_2 will occur). Thus tunneling in unsymmetrical $S^{16}O_2$ will not produce any splittings and will only produce shifts. This has been discussed for linear unsymmetrix $X^{16}O_2$ molecules by Redding [25]. The unsymmetric $S^{17}O_2$ molecule will have splittings since ^{17}O is a fermion. Similarly the A_1 and

A_2 rotational levels of NH_3, and the A_1, A_2, F_1, and F_2 rotational levels of CH_4 are not split by inversion tunneling because of the nuclear-spin statistics.

For rigid molecules it is of great practical value to separate the overall selection rule (i.e., that the product of initial and final rovibrational symmetries must contain Γ^*) into rotational and vibrational parts. This enables us to understand which vibrational transitions are active, and to understand the rotational fine structure, in the event of negligible vibration-rotation interaction. For nonrigid molecules it is useful to make the same kind of separation of the overall selection rule into rotational, contortional, and vibrational selection rules, and there are two cases to consider depending on the contortional energy separations. If the contortional energy separations are as low as rotational energy separations (e.g., in molecules with free internal rotation) then each vibrational band will have a lot of "contortional fine structure," which will complicate the band contour. In this case we need to be able to use the MS group to determine the selection rules on the rotational and contortional quantum numbers for each vibrational band in order to understand the "rotational-contortional fine structure" (in the same way that for a rigid molecule we need selection rules on the rotational quantum numbers for each vibrational band to understand the rotational fine structure). This problem is exemplified by the treatment of the dimethylacetylene molecule [7, 26]. The alternative situation is that in which the contortional energy separations are intermediate between the rotational and vibrational energy separations. In this case we can understand the spectrum more simply if we consider the contortional motion to be a (highly anharmonic) vibrational motion of the tunneling molecule and separate the selection rules into rotational and convibrational parts. The lower the contortional energy separations the more the vibrational bands become complicated with contortional structure and the more necessary the first approach becomes. We can demonstrate all of this by lowering the tunneling barrier in our unsymmetric XH_2 molecule in two stages.

In Fig. 16 we show an intermediate barrier potential function for the unsymmetrical XH_2 molecule. The lowest two contortional states correlate with $v_a^{(\ell)} = 0$ and $v_a^{(r)} = 0$ of the rigidly unsymmetric molecule represented in Fig. 14. We now redefine the way that we label these energy levels (such a relabeling possibility will always occur when there is contortional tunneling), and we call them $v_c = 0, 1, 2$, etc., states of the tunneling molecule (this is the total node count in the wavefunction going right through the symmetric configuration and "c" stands for contortion). The symmetries of these contortional states in the $C_{2v}(M)$ group are also given in Fig. 16, and these symmetries can be determined by using the $C_s(M)$ species of Fig. 14 and the $C_s \rightarrow C_{2v}$ correlation table backwards (as discussed by Watson [10]) or by classifying the tunneling contortional wavefunctions directly in the $C_{2v}(M)$ group. The rocontortional and roconvibrational species in the $C_{2v}(M)$ group can be determined from those of the $C_s(M)$ group by

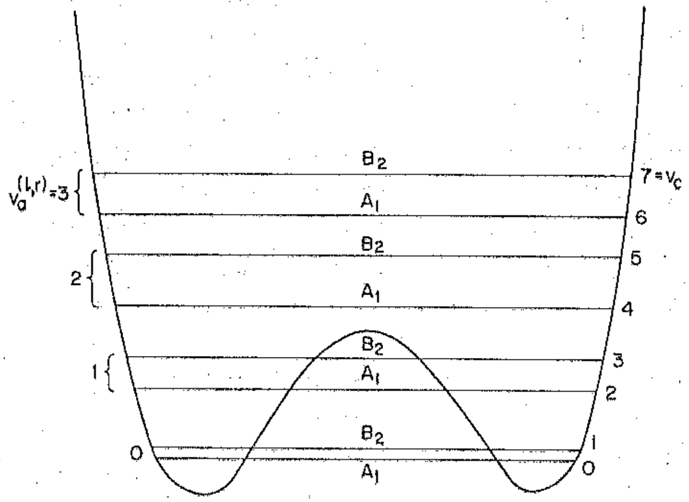

FIG. 16. The J = 0 energy levels of unsymmetrical XH_2 with an intermediate barrier.

correlation. However, now the best way of understanding the vibrational spectrum of the molecule is to consider it as a symmetrical H_2X molecule with a very anharmonic asymmetric stretching vibration. This is the way one would set about solving the rotation-vibration problem [25], and we must set up our group-theoretical approach along the same lines. Using the $C_{2v}(M)$ group we see that the species of μ_a, μ_b, and μ_c are B_2, A_1, and B_1, respectively, and we can understand the activity of the vibrations and the rotational fine structure of the bands just as we understood those of H_2O in the previous sections. However, because of the strong anharmonicity many overtones and combination tones of the asymmetric stretching vibration will be intense. Also hot bands from the $v_c = 1$ state will be strong (since this level has a low energy), and centrifugal distortion effects in the direction of the asymmetric stretch will be large.

Finally we lower the barrier between the left and right forms to zero (keeping the overall curve very "wide") so that the contortional energy separations become comparable to rotational energy separations. We will now study this situation to develop the general principles required to understand the spectrum of a molecule with a zero or near-zero contortional barrier. The molecule now has two regular vibrations (the symmetric stretch and the bend), and the vibrational bands in the spectrum resulting from transitions between the states of the two vibrations will have a complex rotational-contortional fine structure. We need to determine selection rules on v_c, K_a, and K_c for each symmetry type of band. All vibrational states are of symmetry A_1 for this molecule (the asymmetric stretch being the contortion and considered separately); however, for the purpose of generalizing the results, we will allow for vibrational states of any species in the $C_{2v}(M)$ group in the rest of this section. We define Γ_r'', Γ_c'', Γ_v'', Γ_{rc}'', Γ_{cv}'', and Γ_{rcv}'' as the species of the rotational, contortional, vibrational, rocontortional, convibrational, and roconvibrational lower-state levels, respectively, and those for the upper state will be denoted with a single prime, e.g., Γ_r'. For an allowed transition we must have

$$\Gamma_{rcv}'' \times \Gamma_{rcv}' = A_2 \tag{39}$$

in the $C_{2v}(M)$ group. We now want to determine the separate rules on $\Gamma_c'' \times \Gamma_c'$ and $\Gamma_r'' \times \Gamma_r'$ for each possible symmetry of $\Gamma_v'' \times \Gamma_v'$. There are only two possibilities for $\Gamma_c'' \times \Gamma_c'$, namely, A_1 for Δv_c even and B_2 for Δv_c odd. Thus, for example, if $\Gamma_v'' \times \Gamma_v' = A_1$ we can <u>either</u> have $\Gamma_c'' \times \Gamma_c' = A_1$ and $\Gamma_r'' \times \Gamma_r' = A_2$ [since $\Gamma_r'' \times \Gamma_c'' \times \Gamma_v'' = \Gamma_{rcv}''$, $\Gamma_r' \times \Gamma_c' \times \Gamma_v' = \Gamma_{rcv}'$, and $\Gamma_{rcv}'' \times \Gamma_{rcv}' = A_2$ from Eq. (39)] <u>or</u> $\Gamma_c'' \times \Gamma_c' = B_2$ and $\Gamma_r'' \times \Gamma_r' = B_1$. The similar restrictions for $\Gamma_v'' \times \Gamma_v' = A_2$, B_1, or B_2 can be determined, and these are collected together in Table 17. The two bracketed transitions in Table 17 are forbidden because $\Gamma_{cv}' \times \Gamma_{cv}''$ does not equal $\Gamma(\mu_a)$, $\Gamma(\mu_b)$, or $\Gamma(\mu_c)$ (i.e., B_2, A_1, or B_1). However, the forbidden transitions do not result in any vibrational bands being forbidden, just some of the contortional fine structure in some of the bands is forbidden. We will discuss this point in more detail later on.

We can convert the symmetry restrictions of Table 17 to selection rules on the rocontortional quantum numbers for each vibrational band. If $\Gamma_c'' \times \Gamma_c' = A_1$ then Δv_c must be even and if $\Gamma_c'' \times \Gamma_c' = B_2$ then Δv_c must be odd. The rules on ΔK_a and ΔK_c follow from the species of $\Gamma_r'' \times \Gamma_r'$ by using the results of Table 5. These selection rules are collected together in Table 18. We would be inclined to say that we can neglect transitions with Δv_c, ΔK_a, and ΔK_c greater than 1 since for a rigid symmetric rotor and harmonic oscillator such transitions have no intensity. However, contortional motions are highly anharmonic and also allow large centrifugal distortions so that such limits on Δv_c, ΔK_a, and ΔK_c might sometimes be unsatisfactory.

We now want to understand these selection rules in terms of "active" and "inactive" vibrations. In Fig. 17 some convibrational energy levels are drawn; v_n is the quantum number for a vibration

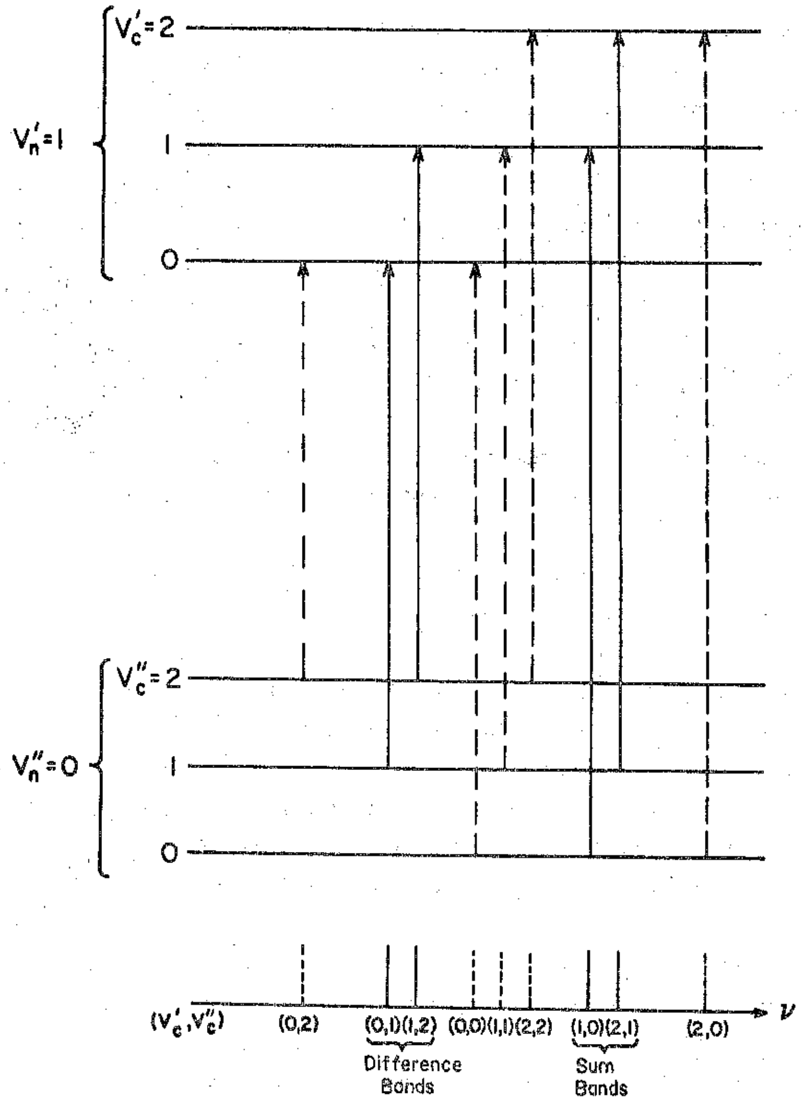

FIG. 17. The contorsional fine structure (Δv_c) on an A_2 fundamental band, i.e., the $v_n' = 1 \leftarrow v_n'' = 0$ band.

of A_2 symmetry and v_c is the contortional quantum number. If the contortional energy separations were large then an A_2 fundamental band would be forbidden (the $v_c' = 0 \leftarrow v_c'' = 0$ band is forbidden), but there would be allowed combination tones (the sum and difference bands). When the contortional energy separations are reduced to a rotational separation these sum and difference bands move close together (and their intensity increases) to give contortional fine structure on the A_2 fundamental. We now have to say that the A_2 fundamental band is allowed with Δv_c = odd selection rules. We really have to discard much of the concept of active and inactive vibrations and work with the symmetry restriction that $\Gamma_{cv}' \times \Gamma_{cv}''$ must be the same as that of μ_x, μ_y, or μ_z <u>after</u> determining the selection rules on v_c and the rotational quantum numbers by using the MS group. This then restricts the allowed contortional lines within some of the vibrational bands. Even this rule will break down in the event of Coriolis mixing of rotation and convibration.

Obviously as the barrier between left- and right-handed XH_2 is pushed to zero and the potential curve closed up (i.e., the contortional force constant increased) to give a normal (high) frequency nearly harmonic asymmetric stretching vibration the spectrum must go smoothly to that of the normal symmetric XH_2 molecule. This will happen because as a result of the decrease in the contortional anharmonicity, the contortional overtones and combination tones (i.e., the sum and difference bands of Fig. 17) will weaken and separate and the vibrational bands will become less wide and gain their normal rotational contour. Also as a result of the increase in the contortional force constant the centrifugal distortion effects will become normal (i.e., small). The main aim of studying the spectra of such nonrigid molecules is to try to determine from the spectrum the shape of the contortional potential curve over as wide a range of the contortional coordinate as possible. The interpretation of the rotational energy-level pattern (i.e., the large centrifugal distortion) in terms of the shape of the contortional potential energy curve is also of great interest. I believe that the papers of Hougen, Bunker, and Johns [27], Bunker and Stone [28], and Hoy and Bunker [29] discuss the best general approach to the solution of these problems. This approach has been adapted and applied to formaldehyde [30], ammonia [31], HCNO [32, 33], and HNCO [33].

B. Ammonia

The contortion (inversion) energy levels of the ammonia molecule have many of the characteristics of the antisymmetric stretching energy levels of the unsymmetric XH_2 molecule considered above. In Fig. 18 the inversion energy levels and the inversion

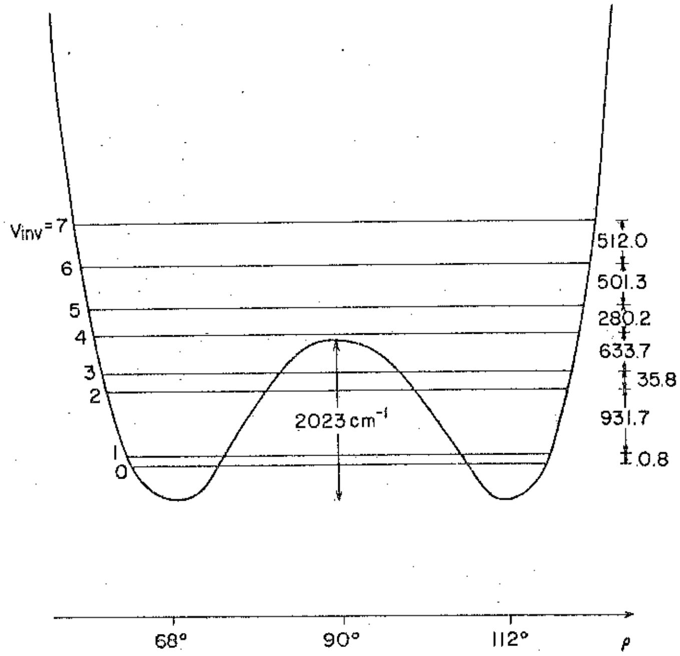

FIG. 18. The inversion energy levels of NH_3. The energy level splittings are in cm^{-1} and the inversion barrier height is from Ref. [31].

potential are drawn [31, 34, 35]. Contrary to the usual custom I have labeled the inversion states according to the number of nodes in the tunneling vibrational wavefunction, and this quantum number is called v_{inv}. The $v_{inv} = 0$ and $v_{inv} = 1$ levels correlate with the $v_{inv}^{(\ell)} = 0$ and $v_{inv}^{(r)} = 0$ levels of the rigidly nonplanar molecule. This way of labeling the vibrational states is introduced in order that we can consider inverting ammonia as a planar molecule with a highly anharmonic out-of-plane vibration (again this is the approach used for solving the vibration-rotation problem [31]). We will treat the ammonia molecule in this way, which allows us to symmetry label the energy levels and determine the vibration and rotation selection rules in a very straightforward way.

The definition of the molecule fixed axes, and the definition of inversion coordinate ρ, for the ammonia molecule in its reference configuration needs some discussion. The reference configuration is that in which all the vibrational coordinates, except ρ, have their equilibrium value. The z-axis is defined as that direction a right-handed screw would travel if twisted in the direction H_1 H_2 H_3. The x-axis is in the z-N-H_1 plane and xyz is right-handed. The angle ρ is the angle between the positive z-axis direction and the bond NH_1. When the molecule is not in its reference configuration,the molecule-fixed axes (i.e. the Euler angles) and ρ are defined by three Eckart and one Sayvets condition.

The MS group of NH_3, when inversion tunneling is allowed for, is the group $D_{3h}(M)$ given in Table A6. The transformation properties of the Euler angles for NH_3(with the z axis being the threefold axis defined by θ and ϕ) are given in Table 19 together with transformation properties of the rotational wavefunction. The species of the symmetric-top rotational wavefunctions of NH_3 in the $D_{3h}(M)$ group are given in Table 20. The species of the normal coordinates are

$$\Gamma(Q) = A_1' + A_2'' + 2E' \qquad (40)$$

where the inversion coordinate is of species A_2''. The K = 2 energy levels of the $v_{inv} = 0$ and $v_{inv} = 1$ vibrational states are drawn in Fig. 19, and the correlation with the energy levels of the rigidly nonplanar molecule is also shown (the symmetry labels for the rigidly nonplanar molecule follow from Table 11). The species of the inversion vibrational coordinate is A_2'', and therefore the rovibrational species of the levels in the $v_{inv} = 1$ state are obtained from Table 20 by multiplying all the species by A_2''.

The nuclear-spin statistics are interesting for NH_3. The species of the overall wavefunction in the $D_{3h}(M)$ group can only be either A_2' or A_2'', and the proton spin species span the representation

$$\Gamma_{NS} = 4A_1' + 2E' \tag{41}$$

The resultant statistical weights of the rotational levels of a

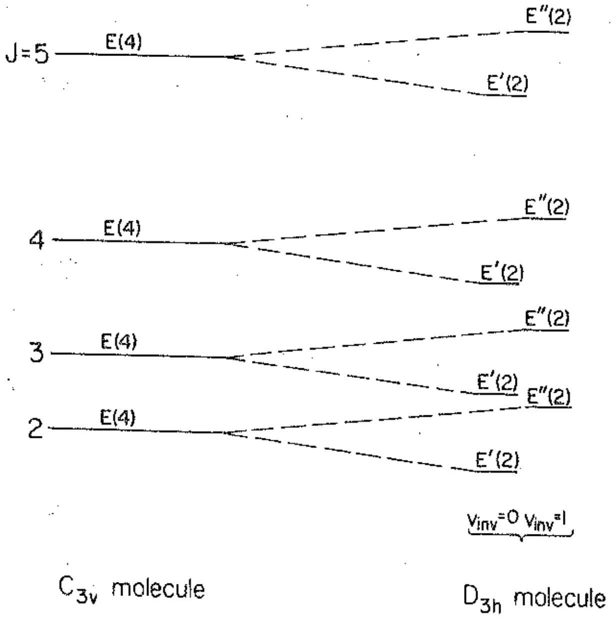

FIG. 19. The energy levels for the K = 2 states of ammonia and the correlation to the rigid (C_{3v}) molecular energy levels. The statistical weights are added in parentheses.

totally symmetric vibrational state have been added in Table 20; rovibrational states of species A_1' or A_1'' are forbidden by the spin statistics. As a result of this, half of the K = 0 energy levels in any given nondegenerate vibrational state of NH_3 are missing, as shown in Fig. 20 for the $v_{inv} = 0$ and $v_{inv} = 1$ states (the states with statistical weight 0 cannot occur). Thus we see that the rovibrational states of rigid NH_3 species A_1 or A_2 in $C_{3v}(M)$ are not split by inversion tunneling. The nuclear-spin statistical weights of all the levels in Figs. 19 and 20 have been added in brackets in the figures.

We now discuss the rovibrational selection rules for NH_3 using the $D_{3h}(M)$ group. The species of Γ^* is A_1'', and thus rovibrational transitions connected by A_1'' with $\Delta J = 0$ or ± 1 are group-theoretically allowed. The species of μ_z is A_2'' and that of (μ_x, μ_y)

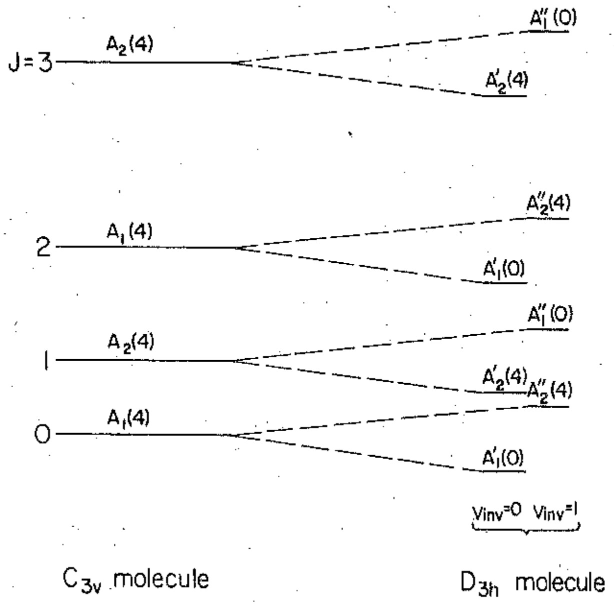

FIG. 20. The energy levels for the K = 0 states of ammonia and the correlation to the rigid molecule (C_{3v}) energy levels. The statistical weights are added in parentheses, and we see that levels with a rovibrational species of A_1' or A_1'' are forbidden.

is E'. Thus vibrational (*including* inversion) transitions are allowed if $\Gamma'_v \times \Gamma''_v$ contains A''_2 or E'. Vibrational transitions connected by the species A''_2 (i.e., Δv_{inv} = odd transitions for the rigid-rotor harmonic oscillator) will occur with rotational transitions connected by the species A'_2 ($\Delta K = 0$ being the most intense), and vibrational transitions connected by the species E' will occur with rotational transitions connected by E" ($\Delta K = \pm 1$ being the most intense). Since the $v_{inv} = 1$ inversion state is very close to the $v_{inv} = 0$ state, hot transitions from it will be as important as those from the ground ($v_{inv} = 0$) state. In Fig. 21 the lowest rotational levels of the $v_{inv} = 0$, 1, 2, and 3 states are drawn and some of the allowed transitions are marked by solid arrows. The $v_{inv} = 3 \leftarrow 0$ and $v_{inv} = 2 \leftarrow 1$ bands are completely on top of each other in the infrared spectrum, and these bands correlate with the $v_2 = 1 \leftarrow 0$ band of the rigid nonplanar molecule. In the microwave spectrum the $v_{inv} = 1 \leftarrow 0$ and $0 \leftarrow 1$ transitions occur in absorption, and some of these transitions are also marked in Fig. 21; these correlate with pure rotation transitions of the rigidly nonplanar molecule. Rotational transitions within the $v_{inv} = 0$ or $v_{inv} = 1$ states are forbidden, but vibration-rotation interaction (spoiling the goodness of K and the vibrational quantum numbers as labels) can make such forbidden transitions weakly allowed (see Oka et al. [23]); two of these transitions are marked by dotted arrows in Fig. 21 (the selection rules, from Table 20 with $\Gamma^* = A''_1$, are K = odd ↔ even with K = 3n ± 1 in both states *or* K = 3n in both states). Obviously the $v_{inv} = 2 \leftarrow 0$ and $3 \leftarrow 1$ forbidden bands also gain intensity (with the same selection rules on K) by this effect and one of these transitions is also dotted in Fig. 21. In an electric field (Stark effect) rovibrational states connected by the species A''_1 with $\Delta J = 0$ or ± 1 will be mixed. In particular, states with the same K value and with v_{inv} values differing by 1 will be mixed by an electric field, and as a result forbidden transitions with Δv_{inv} even will steal intensity from the allowed transitions having Δv_{inv} odd and will have $\Delta K = 0$.

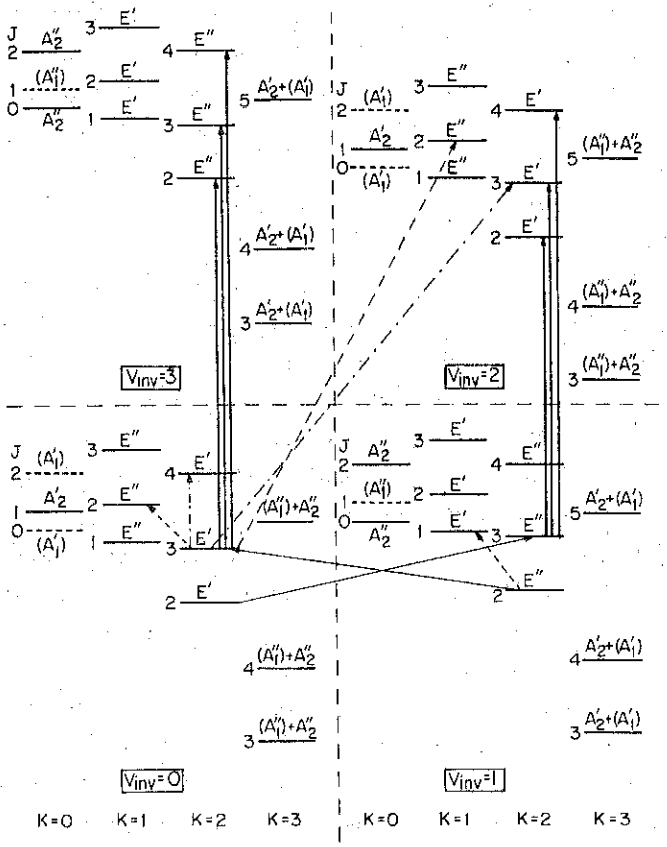

FIG. 21. The lower rotational energy levels of the v_{inv} = 0, 1, 2, and 3 states of NH_3. The $D_{3h}(M)$ symmetry labels have been added and rovibrational states forbidden by nuclear-spin statistics are bracketed. Some of the allowed transitions are marked and a full arrow is used; these transitions satisfy Δv_{inv} = odd and $\Delta K = 0$. Using a dotted arrow some of the forbidden transitions made allowed by nonrigid-rotor effects are marked and these have Δv_{inv} = even, $\Delta K \neq 0$, and $\Delta J = 0, \pm 1$. Forbidden transitions made allowed by applying an external electric field have Δv_{inv} = even, $\Delta K = 0$, and $\Delta J = 0, \pm 1, \pm 2$; two of these are marked with a dot-dash line. For the sake of clarity the energy levels have been spread out and, as a result, the J = 0 levels are not drawn as the lowest.

This manner of labeling the inversion energy levels does help the vibrational spectroscopist, particularly if inversion states above the inversion barrier are seen. This also enables all the energy levels to be unambiguously and simply labeled by vibrational and rotational quantum numbers, and the symmetry designations and selection rules are simple to understand. A detailed determination of the rotational energy-level pattern of several excited states of v_{inv} would be a very worthwhile undertaking.

C. Methanol

The rotorvibrational energy levels and spectrum of methanol have been the subject of an enormous number of investigations. The papers of Kwan and Dennison [36] and Lees [37] are the most recent, and between them they give references to most of the earlier work. We will only discuss the group-theoretical classification of the rotorvibrational (rotational-torsional-vibrational) energy levels and the selection rules using the MS group.

In Fig. 22 our atom-numbering convention and axis-labeling convention are given. The abc axes are principal axes of the molecule when all bond lengths and angles (except the torsion) have

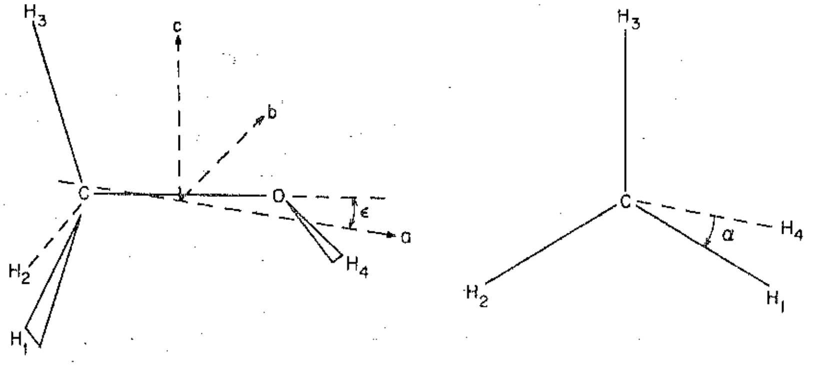

FIG. 22. The atom-numbering convention for methanol and the location of the abc principal axes. The torsional angle α and the tilt angle ε are also defined.

their equilibrium values. The ab axes are in the C-O-H_4 plane, and the orientation of the abc axes in space is given by the Euler angles θ, ϕ, and χ (see Fig. 5). The a axis and the C-O axis are at an angle ε to each other; if the atom H_4 were replaced by a deuterium atom this angle would obviously increase. We define the torsional angle α as the angle between the O-H_4 and C-H_1 bonds measured in the sense shown in Fig. 22. When the molecule is not in this reference configuration the angles θ, ϕ, χ, and α are defined by Eckart [47] and Sayvetz [48] conditions.

The molecular symmetry group of this molecule, when we allow for torsional tunneling, is the $C_{3v}(M)$ group of Table A3. The transformation properties of the angles θ, ϕ, χ, and α under the operations E, (123), and (12)* are given in Table 21. Notice that (θ, ϕ, α) transform like (θ, ϕ, χ) of CH_3F in its $C_{3v}(M)$ group (see Table 9), and, with the identifications (123) = E and (12)* = E*, (θ, ϕ, χ) transform like (θ, ϕ, χ) of H_2O in its $C_{2v}(M)$ group (see Table 1).

The zeroth-order rotorsional wavefunctions [36] can be taken as the product of symmetric-top (K_a) rotational wavefunctions and free internal rotor torsional wavefunctions:

$$\psi^0_{rt} = S_{Jk_aM}(\theta,\phi)\ \exp(ik_a\chi)\ \exp(im\alpha) \tag{42}$$

From the results of Table 21 we can determine the transformation properties of the rotational part of the wavefunction (and of the $|Jk_cM\rangle$ rotational wavefunctions) in the $C_{3v}(M)$ group; the symmetry species of the asymmetric rotor functions are given in Table 22. The rotational species correlate with those of H_2O and the correlation from H_2O to CH_3OH is (A_1, A_2, B_1, B_2) with (A_1, A_2, A_2, A_1). We could, of course, also classify these asymmetric rotor functions in the four-group (a near-symmetry group). The species of the torsional wavefunctions in the $C_{3v}(M)$ group are given in Table 23. These results are similar to the results in Table 11, which are the rotational species for CH_3F.

We now want to correlate the zero-barrier torsional states with the high-barrier energy levels. For rigid staggered methanol, with the H_4 atom between H_1 and H_2, the MS group is [E, (12)*]; this $C_s(M)$ group is given in Table A7. The torsional coordinate has the species A" in this group, and consequently the species of the torsional wavefunction is A' if the torsional quantum number v_t is even and A" if v_t is odd. The correlation of C_{3v} and C_s species is given in Table A14 in the Appendix of Wilson, Decius, and Cross [12], and using this table backwards (Watson [10]) we deduce that A' states correlate with A_1 + E of C_{3v} and A" states correlate with A_2 + E. The correlation diagram is drawn in Fig. 23. Thus for an arbitrary barrier height the torsional states will occur in the order A_1, E, E, A_2, A_1, E, E, A_2, A_1, E, · · ·; these species must be multiplied by the appropriate rotational species from Table 22 to give the rotorsional species.

Now we look at the species of the vibrational states. Using the $C_{3v}(M)$ group, and excluding α, the species of the 11 independent internal coordinates is

$$\Gamma^0(Q) = 5A_1 + 3E \tag{43}$$

The three degenerate vibrations are the perpendicular methyl group vibrations, and the degeneracy of each is lifted by interaction with the hydroxyl group. We will then get in-plane and out-of-plane perpendicular methyl vibrations. The perpendicular C-H stretching vibration has in-plane ($S^{(i)}$) and out-of-plane ($S^{(o)}$) symmetry coordinates that can be written

$$\begin{aligned} S^{(i)} &= \delta r_1 \cos\alpha + \delta r_2 \cos(\alpha + \tfrac{2\pi}{3}) + \delta r_3 \cos(\alpha + \tfrac{4\pi}{3}) \\ S^{(o)} &= \delta r_1 \sin\alpha + \delta r_2 \sin(\alpha + \tfrac{2\pi}{3}) + \delta r_3 \sin(\alpha + \tfrac{4\pi}{3}) \end{aligned} \tag{44}$$

The transformation properties of these coordinates in $C_{3v}(M)$ can be determined as shown in Table 24. We deduce that the species of the three in-plane coordinates is A_1 and that the species of the three out-of-plane coordinates is A_2. Thus, allowing for the lifting of the degeneracies we have

$$\Gamma(Q) = 8A_1 + 3A_2 \tag{45}$$

The species of any vibrational wavefunction can thus be obtained. We can write down the species of any rotorvibrational wavefunction by multiplying the appropriate species of Table 22, Fig. 23, and Eq. (45).

Allowed dipole selection rules occur between states connected by the $C_{3v}(M)$ species $\Gamma^* = A_2$. For transitions within the (ordinary) vibrational ground state or for transitions between totally symmetric vibrational states we must have (for freely twisting methanol):

$$\Gamma'_{rt} \times \Gamma''_{rt} = A_2$$

that is,

$$\Delta|m| = 0, \quad \Delta K_c = \pm 1, \quad \Delta K_a = 0, \pm 1 \tag{46}$$

where we ignore the very weak symmetry-allowed transitions for which the quantum number changes are larger than unity. For transitions to the first excited state of an A_2 vibration or for transitions between vibrational states whose species are connected by A_2 we must have

$$\Gamma'_{rt} \times \Gamma''_{rt} = A_1$$

that is,

$$\Delta|m| = 0, \quad \Delta K_c = 0, \quad \Delta K_a = 0, \pm 1 \tag{47}$$

The selection rules for rigid methanol are known, and we can thus understand them at any intermediate barrier height.

Torsional transitions that are allowed when there is an intermediate barrier height can be of three types: (a) $A_1 \leftrightarrow A_1$, with $\Delta K_c = \pm 1$, $\Delta K_a = 0, \pm 1$, (b) $A_1 \leftrightarrow A_2$, with $\Delta K_c = 0$, $\Delta K_a = 0, \pm 1$, (c) $E \leftrightarrow E$, with $\Delta K_c = 0, \pm 1$ and $\Delta K_a = 0, \pm 1$.

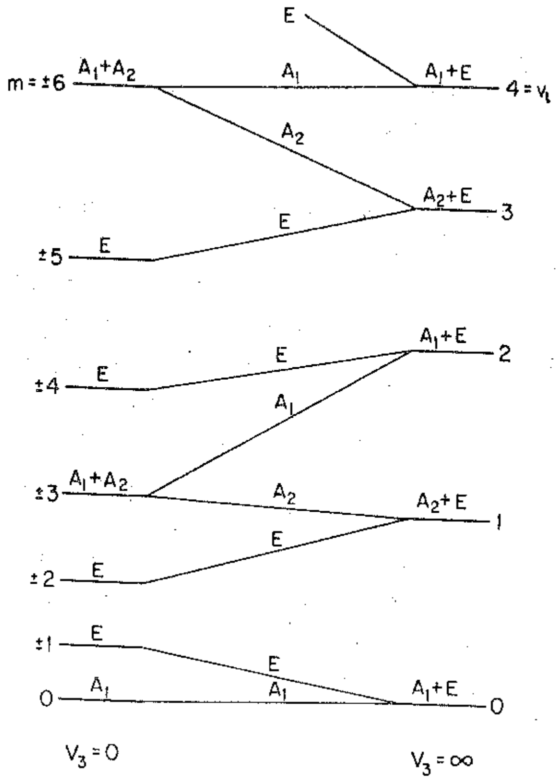

FIG. 23. The correlation of the torsional energy levels from zero barrier to infinite barrier for methanol. Allowed torsional transitions are $A_1 \leftrightarrow A_1$ (with $\Delta K_c = \pm 1$), $A_1 \leftrightarrow A_2$ (with $\Delta K_c = 0$), $E \leftrightarrow E$ (with $\Delta K_c = 0, \pm 1$), all with $\Delta K_a = 0, \pm 1$.

D. Acetone

The energy levels, selection rules, and symmetry properties of molecules with two torsionally tunneling methyl groups attached to a nonlinear frame have been the subject of many papers [38-46]. I will classify the rotational, torsional, and vibrational states of acetone in the MS group and use the results to determine the IR selection rules when torsional tunneling is important. None of the earlier papers have attempted to classify the rotational, torsional, and vibrational wavefunctions of acetone in one symmetry group, and most use a symmetry group of the rotorsional Hamiltonian (a near-symmetry group of the total Hamiltonian) to classify the rotorsional states. This near-symmetry group is isomorphic to the MS group.

The atom-numbering convention used for acetone is shown in Fig. 24. All the bond lengths and bond angles have their equilibrium values in this figure except for the torsional angles, which are arbitrary. When the molecule is in this configuration the molecule-fixed axes are the principal axes, and following Swalen and Costain [41] we label them as shown in Fig. 24. The orientation of these abc axes in space is given by the three Euler angles θ, ϕ, and χ. The two torsional angles α_a and α_b are defined as the angles from the CO bond to the C_a-H_1 and C_b-H_4 bonds, respectively, in the sense indicated in the figure. When the bond lengths and bond angles do not have the equilibrium values then the Euler angles are best defined by using the Eckart condi-

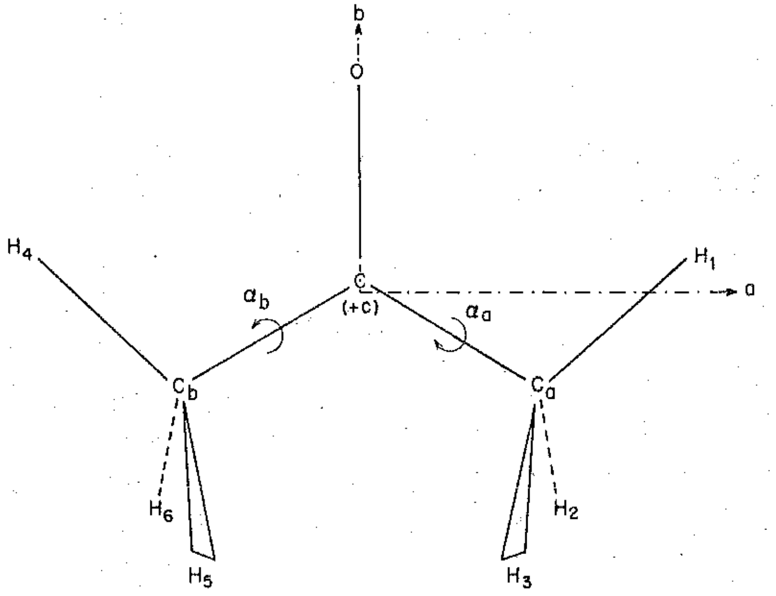

FIG. 24. The atom-numbering convention and axis convention used for acetone. The arrows defining α_a and α_b pass over the C-C bonds.

tions [47]. It is not always appreciated that it is best to use the Eckart conditions, since their use minimized the Coriolis-coupling interactions of rotation and vibration. Similarly the two torsional angles are best defined (when the bond lengths and angles do not have their equilibrium values) by two Sayvetz conditions [48], which similarly minimize the "Coriolis"-coupling interactions of torsion and vibration. In quantitative studies of rotor-vibrational energy-level patterns, and particularly in the study of the variation of the rotational-torsional energy-level pattern between different vibrational states, it is best to use the Eckart and Sayvetz conditions to define θ, ϕ, χ, α_a, and α_b. However, for the purpose of making symmetry classifications of rotational, torsional, and vibrational states we can consider the transformations of, and displacements from, the reference configuration of Fig. 24.

The MS group of acetone is the Group G_{36} given in Table 12 of the paper by Longuet-Higgins [1]. This is given in Table A8 here and the rotorsional near-symmetry group, of the same structure, was obtained by many of the earlier workers. The MS group is the direct product of two groups of order 6 and these are

$$\begin{array}{lll} E & (123)(465) & (14)(25)(36)(ab) \\ & (132)(456) & (15)(26)(34)(ab) \\ & & (16)(24)(35)(ab) \end{array} \qquad \text{(i)}$$

and

$$\begin{array}{lll} E & (123)(456) & (14)(26)(35)(ab)^* \\ & (132)(465) & (15)(24)(36)(ab)^* \\ & & (16)(25)(34)(ab)^* \end{array} \qquad \text{(ii)}$$

Each of these groups is isomorphic with the point group C_{3v}, and it is tempting to give a simple geometric interpretation to the fact that the MS group of acetone factors into the product of two groups each isomorphic with the point group of one methyl rotor. This is an accident and will not occur for a molecule with two rotors each having C_{nv} symmetry with n even, as we shall see in Sec. IV.F, where we consider Y_2XXY_2 and Y_4XXY_4 molecules.

We want to use the group G_{36} to determine the transformation properties of θ, ϕ, χ, α_a, and α_b (and hence of the rotational torsional wavefunctions) and of the normal coordinates Q_r (and thus the species of the vibrational wavefunctions). As shown by Hougen [7] each element of the group G_{36} can be expressed as a product of the four operations (the generators) (123), (456), (14)(26)(35)(ab)*, and (23)(56)*. We need only determine the effect of each of these four elements on θ, ϕ, χ, α_a, α_b and the Q_r in order to be able to determine the effect of all elements of G_{36}. The transformation properties of θ, ϕ, χ, α_a, and α_b (where the a axis is defined by θ and ϕ) under the effect of the four operations are given in Table 25. As a result of this we can determine the species of the $|Jk_aM\rangle$ symmetric top basis-set functions for acetone and the species of the free internal rotor torsional functions

$$\psi_t = \exp(im_a\alpha_a)\ \exp(im_b\alpha_b) \tag{48}$$

where m_a and m_b are positive or negative integers and are the free internal rotation quantum numbers. The classification of the $|Jk_cM\rangle$ symmetric-top basis-set functions proceeds by determining the transformation properties of the Euler angles θ, ϕ, and χ with the c axis defined by θ and ϕ (as done for the H_2O molecule). As a result of these considerations the asymmetric-top rotational functions and the free internal rotation functions have the symmetry species given in Tables 26 and 27. The classification of the rotational wavefunctions in the $C_{2v}(M)$ group of Table A9 can be made; these results (applicable if there is no tunneling) are also given in Table 26, and they are obviously the same as the results obtained earlier for the water molecule.

To determine the species of the normal coordinates we must classify the internal coordinates (really the changes in the internal coordinates) and then subtract any redundant combinations.

There are 22 independent vibrational coordinates (3 x 10 - 6 - two torsional coordinates). The transformation properties of these coordinates and of the redundant combinations under the effects of the generators can be determined, and we deduce that the species of the normal coordinates are

$$\Gamma^0(Q) = 5A_1 + A_2 + 4A_4 + 3G \tag{49}$$

These vibrational species have been deduced with the approximation of there being no coupling of the perpendicular methyl group vibrations through the heavy atom framework. This is, in fact, neglecting the dependence of the G and F matrices for these 22 vibrations on the torsional angles α_a and α_b. To introduce this torsional dependence we can form in-plane (i) and out-of-plane (o), cis (c), and trans (t) combinations (ic, it, oc, and ot) of these coordinates. These are defined, for the C-H stretch, by the equations

$$\begin{aligned} S^{ic} &= S_a^{(i)} + S_b^{(i)} \\ S^{it} &= S_a^{(i)} - S_b^{(i)} \\ S^{oc} &= S_a^{(o)} - S_b^{(o)} \\ \text{and} \quad S^{ot} &= S_a^{(o)} + S_b^{(o)} \end{aligned} \tag{50}$$

where

$$\begin{aligned} S_a^{(i)} &= \delta r_1 \cos \alpha_a + \delta r_3 \cos(\alpha_a + \tfrac{2\pi}{3}) + \delta r_2 \cos(\alpha_a + \tfrac{4\pi}{3}) \\ S_a^{(o)} &= \delta r_1 \sin \alpha_a + \delta r_3 \sin(\alpha_a + \tfrac{2\pi}{3}) + \delta r_2 \sin(\alpha_a + \tfrac{4\pi}{3}) \\ S_b^{(i)} &= \delta r_4 \cos \alpha_b + \delta r_6 \cos(\alpha_b + \tfrac{2\pi}{3}) + \delta r_5 \cos(\alpha_b + \tfrac{4\pi}{3}) \\ \text{and} \quad S_b^{(o)} &= \delta r_4 \sin \alpha_b + \delta r_6 \sin(\alpha_b + \tfrac{2\pi}{3}) + \delta r_5 \sin(\alpha_b + \tfrac{4\pi}{3}) \end{aligned} \tag{51}$$

The symmetry species of these coordinates in G_{36} can be determined from the results in Table 25, and we deduce that:

$$\begin{aligned} \Gamma(S^{ic}) &= A_1 \quad (A_1 \text{ in } C_{2v}) \\ \Gamma(S^{it}) &= A_4 \quad (B_2 \text{ in } C_{2v}) \\ \Gamma(S^{oc}) &= A_2 \quad (B_1 \text{ in } C_{2v}) \\ \Gamma(S^{ot}) &= A_3 \quad (A_2 \text{ in } C_{2v}) \end{aligned} \tag{52}$$

Thus, using the coupled coordinates, we deduce that

$$\Gamma(Q) = 8A_1 + 4A_2 + 3A_3 + 7A_4 \tag{53}$$

which correlates with the C_{2v} classification

$$\Gamma(Q) = 8A_1 + 4B_1 + 3A_2 + 7B_2 \tag{54}$$

The effect of raising the torsional barrier will be to produce splittings and shifts of the torsional states. Following Swalen and Costain [41] we write the torsional potential as

$$V = \left(\frac{V_a}{2}\right)(1 - \cos 3\alpha_a) + \left(\frac{V_b}{2}\right)(1 - \cos 3\alpha_b) + V_{ab} \cos 3\alpha_a \cos 3\alpha_b + V'_{ab} \sin 3\alpha_a \sin 3\alpha_b + \text{sixfold and higher terms} \tag{55}$$

This perturbation mixes states having $\Delta m_a = 3, 6, 9, \cdots$ and/or $\Delta m_b = 3, 6, 9, \cdots$, and thus produces both energy-level splittings and shifts. This will spoil the "goodness" of m_a and m_b as quantum numbers. This perturbation is totally symmetric in G_{36} and does not spoil any of the symmetry classifications. Thus for low-barrier acetone, given the values of K_a, K_c, m_a, and m_b, and the 22 vibrational quantum numbers, we can symmetry label any rotorvibrational state in G_{36} using the results of Tables 26 and 27, and the species in Eq. (53).

The statistical weight of any level can easily be determined using the G_{36} group since the overall wavefunction can only have species A_2 or A_4 in G_{36}, and the proton spin species are

$$10A_1 + 6A_4 + 3E_1 + 3E_3 + E_2 + E_4 + 8G \tag{56}$$

The statistical weights of the rotorvibrational states ψ_{rtv} are given in Table 28. These are the same as the results obtained by Bunker [49] for dimethylacetylene and by Myers and Wilson [42] in their Table IX.

We now examine the problem of correlating the high-barrier symmetries of the rigid C_{2v} molecule with those of the low-barrier molecule. If the molecule is rigidly in the conformation of Fig. 24 then its MS group is the $C_{2v}(M)$ group given in Table A9. The correlation of the rotational species and the vibrational species follows simply from the results given in Table 26 and Eqs. (53) and (54). The correlation of the low and high torsional barrier torsional species needs further comment.

The correlation of G_{36} and C_{2v} species has been discussed by Watson [10]; these results are given in Table 29. We need these results in order to correlate the torsional species from low to high barrier. For the high-barrier molecule the torsional states are labeled by the torsional vibration quantum numbers v^+ and v^- and the symmetry coordinates are $S^+ = (\delta\alpha_a + \delta\alpha_b)/\sqrt{2}$ and $S^- = (\delta\alpha_a - \delta\alpha_b)/\sqrt{2}$. The symmetry species in the $C_{2v}(M)$ group of Table A9 are

$$\Gamma(S^+) = A_2$$

and

$$\Gamma(S^-) = B_1 \tag{57}$$

The symmetry species of the lower excited states of these two torsional vibrations of the rigid molecule in the $C_{2v}(M)$ group can be easily determined; these results are given in Table 30. Using the correlation results of Table 29 we can determine the G_{36} species when tunneling between all nine conformers is allowed for; these results are also given in Table 30. Using these results we can construct the correlation diagram for the torsional states as in Fig. 25. This is similar to the figure of Swalen and Costain [41] except that we assume $\nu^+ < \nu^-$ and we do not assume that $\nu^+ = \nu^-$.

For any barrier height we can determine the rotorvibrational species in G_{36} by multiplying the species of Fig. 25 by those of rotation (dependent on K_a and K_c, and obtained from Table 26) and vibration [dependent on the values of the vibrational quantum numbers and obtained from Eq. (53)].

Allowed rotorvibrational transitions are connected by the species A_3 with the restriction that $\Delta J = 0, \pm 1$. The species of μ_b, μ_c, and μ_a are A_1, A_2, and A_4, respectively, and the species of $(\mu_{ax}, \mu_{ay}, \mu_{bx}, \mu_{by})$ is G, where a(x,y) and b(x,y) are xy axes affixed to each methyl group perpendicular to the C-C bonds with ax and bx in the $C\text{-}C\text{-}H_1$ and $C\text{-}C\text{-}H_4$ planes, respectively. The reason for introducing these top-fixed dipole moment components is that it allows us to discuss the perpendicular methyl vibration fundamentals using the uncoupled (G) coordinates if we wish (this possibility is discussed at the end of this section). We are now in a position to determine the rotorsional selection rules for vibrational transitions of any type. For rotorsional transitions between vibrational states of the same symmetry (this will also apply to rotorsional transitions within the vibrational ground state, and the permanent dipole moment is μ_b^0) we must have $\Gamma'_{rt} \times \Gamma''_{rt} = A_3$. This leads to four possibilities.

$$\Gamma'_r \times \Gamma''_r = A_1 \quad \text{with } \Gamma'_t \times \Gamma''_t = A_3, \tag{58a}$$

or

$$\Gamma'_r \times \Gamma''_r = A_2 \quad \text{with } \Gamma'_t \times \Gamma''_t = A_4, \tag{58b}$$

or

$$\Gamma'_r \times \Gamma''_r = A_3 \quad \text{with } \Gamma'_t \times \Gamma''_t = A_1, \tag{58c}$$

or

$$\Gamma'_r \times \Gamma''_r = A_4 \quad \text{with } \Gamma'_t \times \Gamma''_t = A_2 \tag{58d}$$

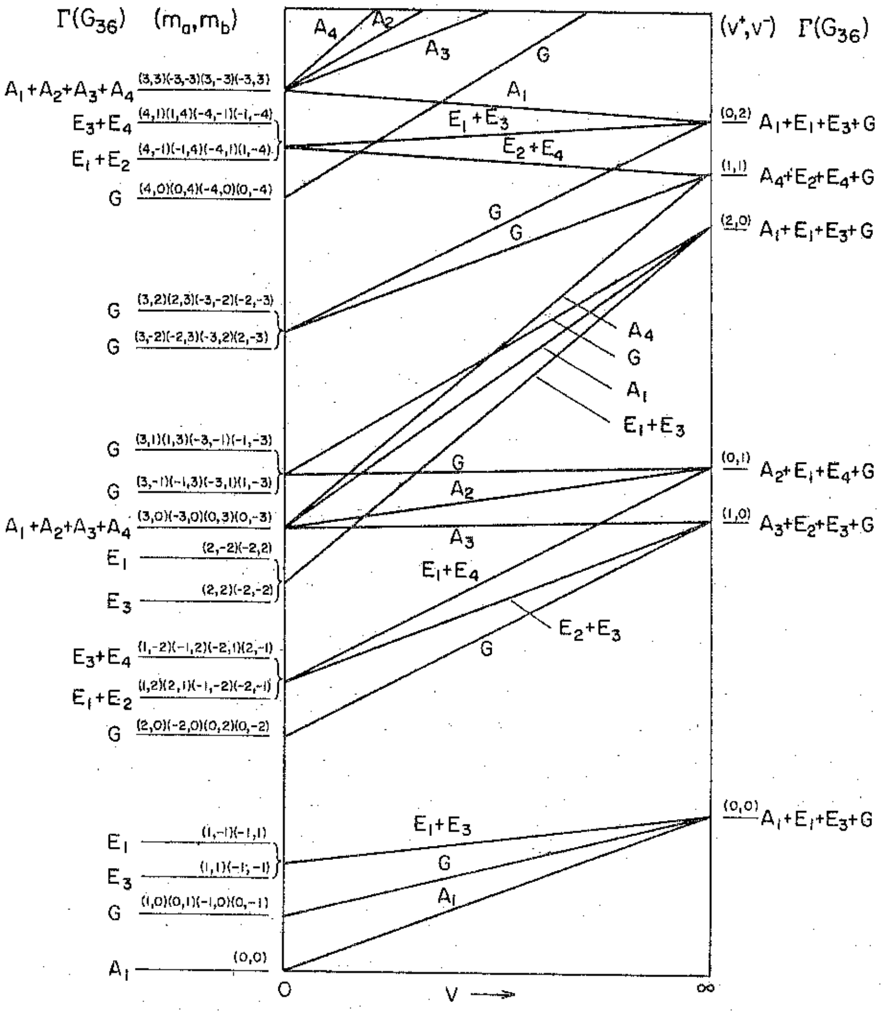

FIG. 25. The correlation of the torsional states of acetone between zero and infinite torsional barriers. The levels on the left are labeled by the quantum numbers (m_a, m_b) and the levels on the right by the quantum numbers (v^+, v^-). The G_{36} species are also added.

Using the symmetry results of Tables 26 and 27 we deduce the following selection rules on rotational and torsional quantum numbers:

$$\Delta K_a = 0,\pm2,\pm4,\cdots,\quad \Delta K_c = 0,\pm2,\pm4,\cdots,$$

$$(\Delta m_a,\Delta m_b) = (0,\pm3),\ (\pm3,0),\ (3,3),\ (-3,-3),\ (3,6),\cdots \tag{59a}$$

or

$$\Delta K_a = 0,\pm2,\pm4,\cdots,\quad \Delta K_c = \pm1,\pm3,\pm5,\cdots,$$

$$(\Delta m_a,\Delta m_b) = (0,\pm3),\ (\pm3,0),\ (\pm3,\pm6),\ (\pm6,\pm3),\cdots \tag{59b}$$

or

$$\Delta K_a = \pm1,\pm3,\pm5,\cdots,\quad \Delta K_c = \pm1,\pm3,\pm5,\cdots,$$

$$(\Delta m_a,\Delta m_b) = (0,0),\ (0,\pm3),\ (\pm3,0),\ (\pm3,\pm3),\cdots \tag{59c}$$

or

$$\Delta K_a = \pm1,\pm3,\pm5,\cdots,\quad \Delta K_c = 0,\pm2,\pm4,\cdots,$$

$$(\Delta m_a,\Delta m_b) = (0,3),\ (3,0),\ (3,-3),\ (-3,3),\cdots \tag{59d}$$

Transitions with K_a, K_c, m_a, or m_b changing by more than one unit will be very weak, and they only gain intensity from vibration-rotation interaction effects that are small. Thus the rotorsional selection rules for transitions within the ground vibrational state (or for transitions between vibrational states of the same symmetry) are obtained from Eq. (59c) to be

$$\Delta K_a = \pm1,\quad \Delta K_c = \pm1,\quad \Delta m_a = \Delta m_b = 0 \tag{60}$$

We can similarly determine the selection rules on K_a, K_c, m_a, and m_b for any of the vibrational bands (dependent on the product of the vibrational species $\Gamma_v' \times \Gamma_v''$); the results are given in Table 31. We have not included transitions for which any of the rotorsional quantum numbers change by more than one unit and this is why we can say that the A_3 vibrations are inactive. The selection rules for the vibrational transitions of rigid acetone are well known, and we can use them in combination with our results to interpret the spectrum at an intermediate barrier situation.

The detailed interpretation of the rotorsional fine structure within each of the three pseudo-fourfold degenerate fundamental bands would be very interesting. There are two ways of going about this analysis. We could use the coupled normal coordinates of the type described by Eq. (50) with symmetries as given in Eq. (52). Three of these coordinates would have infrared-active fundamentals, but the coordinate of species A_3 would have an inactive fundamental. However, Coriolis coupling will mix the four excited vibrational states (the species of the rotations being A_2, A_3, and A_4) and will make the A_3 fundamental active and complicate the rotational fine structure of all the bands. Alternatively, we could use the uncoupled fourfold degenerate normal coordinates and add the end-to-end coupling as a perturbation. Following the work of Bunker and Longuet-Higgins [50] it can be shown that this end-to-end coupling mixes the torsional-vibrational energy levels according to the rules

$$\Delta m_a = \Delta \ell_a = -\Delta m_b = -\Delta \ell_b = \pm 1 \tag{61}$$

where ℓ_a and ℓ_b are the vibrational angular-momentum quantum numbers for each methyl rotor. This can be viewed as a Coriolis coupling of the overall torsional angular momentum and the torsional angular momentum of the vibration. By inference from the work of Olson and Papoușek [51] on dimethylacetylene it is likely that the uncoupled normal coordinates (of G type) will be more easy to use than the coupled normal coordinates from the point of view of interpreting the fine structure. It is likely that the uncoupled coordinates more closely describe the vibrational motion of the molecule.

As a postscript to this section on acetone I might mention why I have carefully avoided writing the torsional wavefunction as the product of the two functions

$$\psi_t^+ = \exp[i(m_a+m_b)(\alpha_a+\alpha_b)/2]$$

and

$$\psi_t^- = \exp[i(m_a-m_b)(\alpha_a-\alpha_b)/2] \tag{62}$$

The reason that I have avoided doing this is that each of these functions is ambiguous if one (and only one) of either m_a or m_b is odd, since in this circumstance each function will change sign if either α_a or α_b is increased by 2π. The product of the two functions is never ambiguous. If we wish to classify each of these wavefunctions we need the double group of G_{36} (in which the effects of this ambiguity is allowed for) and this group will be discussed when we treat dimethylacetylene in the next section. For dimethylacetylene the use of the double group is unavoidable, but for acetone we can avoid ever having to use it by not introducing this separation of the torsional wavefunction.

E. Dimethylacetylene

Many man years have been expended on the problem of the symmetry properties and vibration-rotation spectrum of dimethylacetylene (see Bunker [26] and references therein, Bunker and Hougen [52], Papousek [53], and Olson and Papousek [51]). I will summarize the position that has emerged.

In the treatment of the acetone molecule we could consider the perpendicular vibrations of the rotors to be coupled or uncoupled when we determined the rotorsional selection rules. For nonrigid molecules that have a linear framework, such as dimethylacetylene, there is usually some strong end-to-end coupling (e.g., for the skeletal bending vibrations of dimethylacetylene). When this occurs vibrational states involving excitation of such a coupled vibration must be treated with cis and trans coupled basis functions, and the uncoupled basis set is not useful. To determine rotational and torsional selection rules for transitions to such coupled states it becomes necessary to use an extended molecular symmetry group (EMS group) because of the ambiguous transformation properties inherent in such coupled states. For two-top molecules this EMS group is the double group of the MS group. For the uncoupled vibrational states the MS group suffices, just as it did for acetone. For nonrigid molecules with a linear framework that have inequivalent rotors (e.g., methylsilane) the double group can be avoided since there are no resonances between the perpendicular vibrations of the rotors [54].

In Fig. 26 the atom-numbering convention used for dimethylacetylene is given together with the definition of the rotor-fixed axes. The orientations of the $x_a y_a z$ and $x_b y_b z$ axes relative to space-fixed XYZ axes are given by the Euler angles (θ, ϕ, χ_a) and (θ, ϕ, χ_b), respectively, and we can write the zeroth-order rotation-torsion wavefunctions as

$$\psi_{rt} = S_{JkM}(\theta,\phi) \exp(ik_a\chi_a) \exp(ik_b\chi_b) \tag{63}$$

where k_a and k_b are positive or negative integers and $k = k_a + k_b$. The MS group of dimethylacetylene is the same as that of acetone and is the group G_{36} of Table A8. The transformation properties of

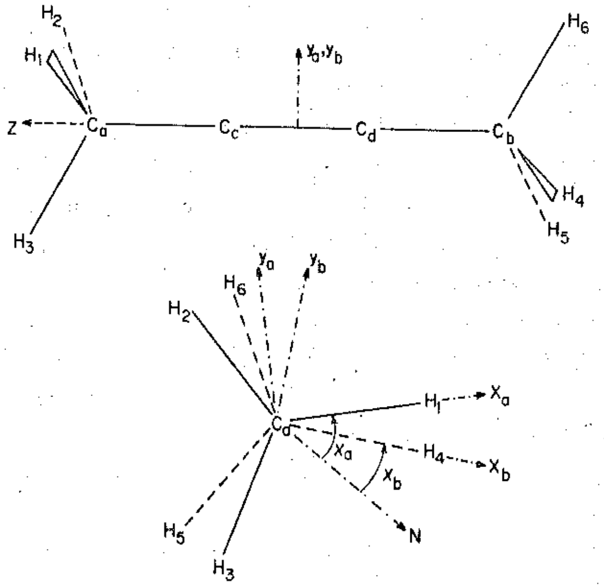

FIG. 26. The atom-numbering convention and definition of rotor-fixed axes for dimethylacetylene.

θ, ϕ, χ_a, and χ_b under the effects of the generators of this group are given in Table 32 and the symmetry properties of the rotorsional wavefunctions are given in Table 33 (note the similarity with Table 27).

In the approximation of ignoring the dependence of the vibrational kinetic and potential energies on the torsional angle (i.e., the dependence of the 23 x 23 G and F matrices on the torsional angle) we deduce that the normal coordinate species is

$$\Gamma^0(Q) = 4A_1 + 3A_4 + 4G \tag{64}$$

Thus in this approximation (i.e., that of neglecting the end-to-end coupling of the $\equiv C_d—C_bH_3$ and $H_3C_a—C_c\equiv$ perpendicular vibrations) we have four fourfold degenerate vibrations, viz.: The C≡C-C bend, the C-H stretch, the CH_3 deformation, and the CH_3 rock. There is good experimental evidence that for the last three vibrations this is a very good approximation. For the degenerate C-H stretch the splitting of this degeneracy is only 0.26 cm^{-1} (Olson and Papousek [51]). The medium resolution spectra of Mills and Thompson [55] show that the end-to-end coupling effects are very small for the CH_3 deformation and CH_3 rocking vibrations. However, for the skeletal bending vibrations the coupling pushes the cis and trans combinations about 170 cm^{-1} apart, and the coupling is clearly not a small perturbation.

If we stick to the approximation of neglecting the end-to-end coupling in our basis functions for the moment, then we determine the selection rules on K_a and K_b for the fundamentals as follows. Allowed rotorvibrational transitions are connected by the G_{36} species $\Gamma^* = A_3$. We can classify the rotor-fixed dipole moment components as $\Gamma(\mu_z) = A_4$ and $\Gamma(\mu_{xa},\mu_{ya},\mu_{xb},\mu_{yb}) = G$ for use with the uncoupled basis set. We deduce that the fundamentals of species A_4 are IR active with $\Gamma'_{rt} \times \Gamma''_{rt} = A_2$ and that the fundamentals of species G are IR active with $\Gamma'_{rt} \times \Gamma''_{rt} = G$. From the symmetry species in Table 33 we see that the A_4 fundamentals are active with the selection rules:

$$\Delta(K_a+K_b) = \Delta(K_a-K_b) = 0$$

$$\text{i.e. } \Delta K_a = \Delta K_b = 0 \qquad (65)$$

and the G fundamentals are active with selection rules

$$\Delta(K_a+K_b) = \Delta(K_a-K_b) = \pm 1$$

$$\text{i.e. } (\Delta K_a,\Delta K_b) = (0,\pm 1) \text{ or } (\pm 1,0) \qquad (66)$$

In both cases I have neglected the very weak symmetry-allowed transitions that have ΔK_a and/or ΔK_b greater than 1 [from symmetry Eq. (65) is 3n and Eq. (66) is 3n ± 1 but only 0 and ±1 are strong]. Using these selection rules the G-fundamental bands will have the appearance of Fig. 2 of Bunker and Longuet-Higgins [50], and this is in good agreement with the experimental results of Olson and Papousek [51] and Mills and Thompson [55] for the degenerate methyl vibrations.

For understanding the detailed appearance of the fundamentals, overtones, and combination tones of the A_4 and methyl G vibrations the theory presented here and in the papers of Bunker and Longuet-Higgins [50] and Papousek [53] is adequate. The end-to-end coupling and torsional barrier provide small perturbations to the fine structure in the bands. The parameters V_1 and V_3 that characterize the extent of the end-to-end coupling and torsional barrier, respectively, can be determined for each vibrational state and for the degenerate C-H stretching fundamental Olson and Papousek [51] have determined that $V_1 = -0.31\ \text{cm}^{-1}$ and $V_3 < 4\ \text{cm}^{-1}$. The interpretation of V_1 in terms of the dependence of the F and G matrices on the torsional angle has not been worked out in detail (but see Bunker and Hougen [52] and Ref. [77]).

To understand the skeletal-bending fundamental band, and overtones and combination tones involving it, it is unfortunately necessary to use the double group of G_{36}. This is because the end-to-end coupling of the skeletal-bending vibrations is very strong, giving cis and trans combinations of widely differing frequencies, and our zeroth-order wavefunction must involve the coupled vibrational coordinates. The coupled vibrational coordinates are cis and trans combinations of the uncoupled coordinates, and they involve the torsional angle as a parameter. The most useful zeroth-order rotorvibrational wavefunctions in the event of strong end-to-end coupling are

$$\psi_{rtv} = S_{JkM}(\theta,\phi)\ \exp(ik\chi)\ \exp(ik_i\gamma)\psi_v[Q_l(\gamma)] \qquad (67)$$

where $k = k_a + k_b$, $k_i = k_a - k_b$, $\chi = (\chi_a+\chi_b)/2$, $\gamma = (\chi_a-\chi_b)/2$, and the 23 normal coordinates can be taken to depend on γ. The cis- and trans-coupled symmetry coordinates are given in Table II of Bunker [26]. We are now interested in classifying separately the rotational, torsional, and vibrational wavefunctions where

$$\psi_r = S_{JkM}(\theta,\phi)\ \exp(ik\chi)$$

$$\psi_t = \exp(ik_i\gamma)$$

and

$$\psi_v = \psi_v[Q_l(\gamma)] \qquad (68)$$

so that we can determine the selection rules on k and k_i for each fundamental.

Let us try to classify ψ_r in G_{36}. To do this we want to determine the effect of the generators of the group and we can write, for example:

$$\begin{aligned}(123)\psi_r &= (123)S_{JkM}(\theta,\phi)\ \exp[ik(\chi_a+\chi_b)/2]\\ &= S_{JkM}(\theta,\phi)\ \exp[ik(\chi_a - \tfrac{2\pi}{3} + \chi_b)/2] \qquad (69a)\end{aligned}$$

or

$$(123)\psi_r = S_{JkM}(\theta,\phi)\exp[ik(\chi + \tfrac{4\pi}{3} + \chi_b)/2] \qquad (69b)$$

From Eq. (69a) we get

$$(123)\psi_r = \exp(-i\pi k/3)\psi_r \qquad (70a)$$

but from Eq. (69b) we get

$$(123)\psi_r = \exp(2\pi ik/3)\psi_r \tag{70b}$$

Thus, for example, for k = 3 we can have either

$$(123)\psi_r = -\psi_r \tag{71a}$$

or

$$(123)\psi_r = +\psi_r \tag{71b}$$

and the transformation properties of ψ_r (and ψ_t and ψ_v) are ambiguous under the effect of any element of the group G_{36}. That is:

$$(123)\chi = \chi - \frac{\pi}{3} \quad \text{or} \quad \chi + \frac{2\pi}{3} \tag{72a}$$

and

$$(123)\gamma = \gamma - \frac{\pi}{3} \quad \text{or} \quad \gamma + \frac{2\pi}{3} \tag{72b}$$

We cannot, therefore, classify these wavefunctions according to the (proper) representations of the MS group G_{36}. Hougen [7] showed how to get around this difficulty by introducing the EMS group (the double group) $G_{36}^{\dagger}$. The EMS group $G_{36}^{\dagger}$ is generated by the four operations A, B, C, and D, where A has the same effect on the spatial coordinates and θ and ϕ as (123) but is defined (we number the H atoms differently from Hougen [7] so these transformation properties are different from those of Hougen) to send χ to $\chi - \pi/3$ (or $\chi + 5\pi/3$) and γ to $\gamma - \pi/3$; B has the same effect on the spatial coordinates and θ and ϕ as (456) but is defined to send χ to $\chi + \pi/3$ and γ to $\gamma - \pi/3$; C has the same effect on the spatial coordinates and θ and ϕ as (14)(26)(35)(ab)(cd)* but is defined to send χ to $-\chi + \pi$ and γ to $-\gamma$; D has the same effect on the spatial coordinates and θ and ϕ as (23)(56)* but is defined to send χ to $-\chi$ and γ to $-\gamma$. The elements all have a well-defined effect on the wavefunctions ψ_r, ψ_t, and ψ_v and, for example, for k = 3:

$$A\psi_r = -\psi_r \tag{73a}$$

whereas

$$A^4\psi_r = \psi_r \tag{73b}$$

The group generated by these operations is the group $G_{36}^{\dagger}$ and this is given in Table I of Hougen [7]. This is exactly analogous to the problem of trying to classify separately the rotational and vibrational wavefunctions of a linear molecule in the MS group. If we wished to follow the notation introduced for linear molecules we could write $A = (123)_{5\pi/3}$ and $A^4 = (123)_{2\pi/3}$, etc. Notice that here there are only two possible values of the subscript ε, whereas for linear molecules any value is possible.

The cis-coupled degenerate coordinates are those of symmetry E_{1d} in $G_{36}^{\dagger}$ given in Table II of Bunker [26] and the trans-coupled degenerate coordinates are those of symmetry E_{2d} in $G_{36}^{\dagger}$ in the same table. The separate species of the rotational and torsional wavefunctions in $G_{36}^{\dagger}$ are given in Table 34 here and the normal coordinate species are (but see [7, 26, 52, and 72]).

$$\Gamma(Q) = 4A_{1s} + 3A_{4s} + 4E_{1d} + 4E_{2d} \tag{74}$$

The species of (μ_x, μ_y, μ_z) (where the xyz axes are defined by θ, ϕ, and χ) is $A_{4s} + E_{1d}$. The selection rules on the fundamentals are deduced to be as given in Table 35. This is the same as Table XI of Bunker [26] but the very weak transitions with ΔK and/or ΔK_i greater than 1 have been omitted. The E_{1d} and E_{2d} fundamentals are very strongly Coriolis coupled and in the event of a near degeneracy (i.e., little end-to-end coupling) it is better to start with the uncoupled basis functions of G symmetry [50].

In conclusion, then, to understand the rotational torsional fine structure on the vibrational bands in the specturm of this molecule we need selection rules on K_a and K_b or on K and K_i. The fine structure in the bands involving excitation of either of the skeletal bends can only be understood in terms of selection rules on K and K_i, and the determination of these results demands the use of the EMS group $G_{36}^{\dagger}$. For all vibrational bands that do not involve the skeletal bends the G_{36} group can be used, and the selection rules on K_a and K_b are given in Eq. (65) and (66). Perturbations involving the skeletal bends and the other vibrations demand the use of the EMS group classification throughout, and it is clear that a complete rotation-torsion-vibration analysis of the spectrum of dimethylacetylene would necessitate the use of the EMS group.

F. Other Nonrigid Molecules

Many other nonrigid molecules have been discussed in the literature, and in this section I will summarize and extend the results obtained. Among the molecules discussed here are B_2F_4, CH_3NO_2, ferrocene, H_2O_2, methylsilylacetylene, and a hypothetical $Y_4X\text{-}XY_4$ molecule.

Ethylenelike and nitromethanelike molecules are discussed in the paper of Papousek et al. [56]. The molecular symmetry group of an ethylenelike molecule that has torsional tunneling is the same as that of hydrazine, and is given in Table 14 of Ref. [1]. This group is isomorphic to the D_{4h} point group and we call it G_{16}. The character table of this group is also given in Table 5 of the paper on B_2F_4 by Finch, Hyams, and Steele [57]. To make a complete study of the rotorvibrational energy levels and selection rules it is necessary to use the EMS (double) group $G_{16}^{\dagger}$ and the character table of this group is given in Table II of the paper by Papousek et al. [56]; this is given in Table A10. Using this group the rotational and torsional wavefunctions [written as in Eq. (63) above] have the species given in Table 36 (the same results are given in [58]). Uncoupled normal coordinates have the species

$$\Gamma^0(Q) = 3A_1^+ + 2B_1^+ + 2E^+ + E^- \qquad (75)$$

in the G_{16} group. The species of coupled coordinates in the $G_{16}^{\dagger}$ group is not unique and this is discussed in Ref. [58]. The uncoupled dipole moment operator components have the following species in G_{16}: $\Gamma(\mu_z) = B_1^+$, $\Gamma(\mu_{xa},\mu_{xb}) = E^+$, and $\Gamma(\mu_{ya},\mu_{yb}) = E^-$, where the x axes are in the CH_2 planes. Allowed rotorvibrational transitions are connected by the species $\Gamma^* = A_1^-$. In this uncoupled approximation the two B_1^+ vibrations will have IR-active fundamentals with selection rules $\Delta K = 0$, the two E^+ vibrations and the E^- vibration will have IR-active fundamentals with selection rules $\Delta K = \pm 1$, $\Delta K_i = \pm 1$. We ignore the symmetry-allowed transitions having K or K_i changing by more than unity. The effect of the end-to-end coupling of the perpendicular methylene vibrations will be to split each of the three E fundamentals into two bands, one of which will lose intensity as a result of the end-to-end coupling. To determine if there is free internal rotation (or a very low barrier) in a molecule of this type it is necessary to resolve some rotational structure in these E bands; at least enough to detect the presence of torsional fine-structure broadening effects.

The MS group of nitromethanelike molecules have been discussed in the papers of Longuet-Higgins [1] and Papousek et al. [56]. The molecular symmetry group is given in Table 1 of Longuet-Higgins' paper, and the EMS (double) group of this group is given in Table VI of the paper by Papousek et al. [56]. I give the character table of the MS group in Table A11 and call it G_{12}. I feel that the introduction of the EMS group is unnecessary. In the uncoupled representation the normal coordinates span the representation

$$\Gamma^0(Q) = 5A_1' + 2A_1'' + A_2'' + 3E' \tag{76}$$

If we allow for the splitting of the degeneracies of the perpendicular methyl group vibrations by the heavy-atom frame [see Eq. (44) above] we get

$$\Gamma(Q) = 5A_1' + 5A_1'' + 4A_2'' \tag{77}$$

The symmetry coordinates are discussed in Papousek et al [56].

The classification of the rotational and torsional wavefunctions of a nitromethanelike molecule in G_{12} has been discussed by Longuet-Higgins [1], and he introduced the useful concept of "equivalent rotations". Since CH_3BF_2 and CH_3NO_2 are near-oblate asymmetric rotors we classify the $|Jk_c>$ symmetric-top basis functions. The symmetry species of these functions and the species of the torsional functions are given in Table 37. The effect of asymmetry is to split all the K_c degeneracies, and the reader should, by now, be able to work out the species of the $|J_{K_aK_c}>$ functions.

An allowed rovibrational transition is connected by the G_{12} species $\Gamma^* = A_2'$. The dipole moment components for a nitromethane-like molecule, along axes fixed to the heavy-atom frame have the following species: $\Gamma(\mu_c) = A_2''$, $\Gamma(\mu_a$, along C-N) = A_1', $\Gamma(\mu_b) = A_1''$. We do not need to consider any "associate element of C_{2v}" in order to obtain these results, although it was used by Longuet-Higgins [I] and may be of some pedagogic help. We can use the results of Eq. (77) and Table 37 to deduce that the five A_1' fundamental bands will be IR active with selection rules $\Delta K_c = \pm 1$, $\Delta K_i = 0$; the five A_1'' fundamentals will be IR active with selection rules $\Delta K_c = \pm 1$, $\Delta K_i = 0$, and the four A_2'' fundamentals will be IR active with selection rules $\Delta K_c = 0$, $\Delta K_i = 0$. If it is convenient for the analysis of the band to consider a perpendicular methyl vibration to be degenerate (species E') then the selection rules are $\Delta K_c = 0, \pm 1$ with $\Delta K_i = \pm 1$. As well as CH_3BF_2 and CH_3NO_2, the CH_3NH_2 molecule also has the MS group G_{12} since both inversion and twisting occur.

Ferrocene has been discussed by this author before [49, 59]. The MS group G_{100} is given in [49] and the EMS (double group) $G_{100}^{\dagger}$ is given in [59]. Using the $G_{100}^{\dagger}$ group the species of the normal coordinates can be written

$$\Gamma(Q) = 4A_{1s} + A_{2s} + A_{3s} + 4A_{4s} + 5G_{1s} + 6G_{4s} + E_{6d} \tag{78}$$

where it is obviously only necessary to use a coupled (E_{6d}) coordinate for the ring-metal-ring bending. The rotational and torsional species, and approximate descriptions of these vibrational coordinates are given in [59]. As shown in [59] allowed rotorvibrational transitions are connected by the species A_{3s}, and the selection rules on the fundamental bands are as follows: The A_{4s} fundamentals are IR active with selection rules $\Delta K = 0$ and $\Delta K_i = 0$; the G_{1s} fundamentals are IR active with selection rules $\Delta K = \pm 1$ and $\Delta K_i = \pm 1$; and the E_{6d} fundamental is IR active with selection rules $\Delta K = \pm 1$ and $\Delta K_i = 0$. There will thus be 10 IR-active fundamentals. The activity of the fundamental in the Raman spectrum has also been considered [59]. The very simple observed solution spectra of ferrocene (Hartley and Ware [60]) can be much better fitted by these simple results than by those obtained for an assumed staggered-ring D_{5d} configuration.

Methylsilylacetylene and methylsilane have been discussed by Bunker [54], Hougen [61], Bunker and Hougen [52], and Hirota [62]. The MS group is a group of 18 elements G_{18} given in Table 1 of Bunker [54], and although the EMS (double) group was introduced by Hougen [61] I think that its use can be avoided. For methylsilylacetylene, if we ignore the end-to-end coupling (i.e., add it as a perturbation to the rotorvibrational levels), the species of the normal coordinates is

$$\Gamma^0(Q) = 7A_1 + 4E_1 + 4E_2 \tag{79}$$

in G_{18}. The seven A_1 vibrations will give rise to IR parallel fundamentals, and the eight degenerate vibrations will give rise to perpendicular fundamentals. Hirota [62] has used G_{18} in his microwave study of methylsilane.

The character tables of the MS groups of $C(CH_3)_4$ and $M(NH_3)_6$, when torsional tunneling is allowed for, have been determined by Stone [63]. These groups have 1944 and 34,992 elements, respectively, and the character tables were obtained by computer trial and error generation of representations using appropriate basis-set functions.

The puckering spectrum of cyclobutane has been discussed with the help of its MS group (isomorphic to the D_{4h} point group) by Stone and Mills [64]. Mills [65] has discussed cyclopentane with the help of its MS group (isomorphic to the D_{5h} point group).