

Molecular Symmetry Group as Applied to the Spectroscopy of Molecules with Methyl Groups: Toluene, Nitromethane, and 5-Methyltropolone's

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A theory of the molecular symmetry group (MSG) is presented to describe the spectroscopy of molecules that consist of methyl (top) and planar (frame) groups and belong to the G_{12} MSG. This was done in a form of Fourier-series expansion on the torsional angle of the methyl group concerning its two kinds of coupling terms, by choosing three kinds of systems in the title: (1) A morphing technique to describe the vibronic coupling is applied to interpret the torsionally induced $S_1 \leftarrow S_0$ absorption spectra of toluene (as partially described in a recent Letter). (2) The torsion–vibration coupling term in the top (through its interaction with the frame) was confirmed to split the degenerate e' levels of either vibrational or torsional modes into either $a_1'' + a_2''$ levels/modes or $a_1' + a_2'$ levels, respectively. The latter was made with the interpretation of either broad IR absorption spectra of nitromethane or peculiar low-frequency bands in the electronic spectra of 5-methyltropolone, respectively.

The molecular point group (MPG), whose elements are rotations and reflections of vibronic variables, is traditionally used when studying the vibronic levels of a molecule in a given electronic state that has a unique equilibrium configuration with no observable tunneling between configurations (of a rigid molecule). When studying rovibronic levels of a (polyatomic) molecule, however, the present molecular symmetry group (MSG), whose elements consist of the permutations of identical nuclei with or without inversion, has to be consulted, the presence of a unique equilibrium configuration being immaterial. These are what are stated in a famous textbook by Bunker and Jansen.[1] Actually, most current researchers, who appealed to the MSG, utilized prescriptions (terminology, notations, character tables, and so on), as offered in Ref. 1. The present author is not an exception, who invoked the MSG while investigating the rotational effect on a radiationless transition in such as pyrazine[2] and on the channel 3 decay in benzene (involving pre-isomerization),[3] and advocated it while trying to publicize their results. The spectroscopist, who is concerned with nonrigid molecules such as the title system (and rovibronic levels), is urged to appeal to the MSG. Also to be noted is the fact that no unified formalism is available for the application of MSG to the molecular spectroscopy (in contrast to the conventional theory, such as vibronic coupling (VC) with Taylor-series (T-S) expansion), the number of formalisms being as many as that of molecules under discussion. This will be shown to be evident even for the restricted kind of molecules, as described in this paper. (Especially in this field, wisdom is predominant over a bunch of scrappy knowledge.)

A brief description will be given of the peculiarity in the title system, which consists of methyl (top) and planar (frame) groups. One of relative vibrations of the top to the frame may be classified into the two limits: (1) the free-rotor limit, to be described as an internal rotation whose frequency is below 100 cm^{-1}, and (2) the hindered-rotor limit, to be described as a torsion whose frequency is more than 100 cm^{-1}. In the case of the former, it is nothing but the large-amplitude mode. However, in the case of the latter, tunneling is expected through the not-so-significant potential barrier due to a minor steric hindrance by the frame. Therefore, the title system has to be described with the MSG not withstanding the frequency of the torsional mode, the terminology to be used throughout this paper.

In a recent Letter,[4] the author proposed a new method of Fourier-Series (F-S) expansion to describe the VC involving a torsional mode of a methyl group, and successfully interpreted the Franck-Condon (FC)/symmetry forbidden m_0^{3+} band in the allowed $S_1 \leftarrow S_0$ transition of toluene as intensity borrowing from the $S_2 \leftarrow S_0$ transition. This is based on the idea to describe the VC as nuclear-coordinate dependence of the electronic transition moment on the AO-following-nuclei approximation, as proposed earlier.[5] However, due to page restriction, an explicit nuclear-coordinate dependence was taken into account only for the torsional mode (ρ), others being treated in the forms of effective averages.[4–6] Therefore, one of the purposes of this paper is to give a clearer description, e.g. by a detailed derivation of its Eq. 9. It can be most adequately described with the terminology of "morphing".[6] However, the purpose of this paper is not merely restricted to the VC, but rather to present a general discussion as a supplement (modification, expansion, and correction) of the authoritative review article (concerning the nonrigid molecule, of more than 70 pages) by Bunker and Jensen (Chap. 15 of Ref. 1), so that such as the title systems can adequately be described. (This article is practically the only comprehensive textbook of more than 700 pages which describes MSG). For example, the F-S expansion is shown to be the most useful devise, e.g. in describing torsion–vibration coupling (TVC), in contrast to such as the conventional Herzberg–Teller (H–T) theory based on T-S expansion. Hereafter, three kinds of coupling terms are distinguished with abbreviations of obvious meanings, as clarified below: (1) VEC (coupling between electronic and vibrational

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motions), (2) TEC (coupling between electronic and torsional motions), and (3) TVC (coupling between vibrational and torsional motions). Accordingly, conventional VC is regarded to represent both VEC and TEC, the latter representing the present case of toluene.

In Section 1 of Theory, a general consideration is made for describing the above-mentioned coupling terms while taking the G_{12} MSG as an example. Then, in Section 2 of Application, three kinds of systems are picked up as Abstracted. The spectral data to be interpreted are: (1) the forbidden m_0^{3+} band in the allowed $S_1 \leftarrow S_0$ transition of toluene, as was observed first by Murakami et al.,[7] and was cited in a review article (section 15.4.3 of Ref. 1). The latest paper for this system appears to be that by Borst and Pratt.[8] (2) Extremely broad (and structured) bands in the IR spectrum of nitromethane (NMn) vapor, as allocated to degenerate e' modes.[1,9–13] (3) Peculiar torsional bands in the electronic spectra of 5-methyltropolone's (MTrn's, belonging to G_6 and G_{12} MSGs), i.e. an apparent splitting of the "2E" levels (only) in MTrn (inconsistent with the group-theoretical assignment of e'), as was observed, but was "hardly" interpreted by Nishi et al.,[14,15] (Their temporary interpretation is the coupling between torsion and proton tunneling, though no corresponding scheme for the splitting is presented explicitly.) In the last case, another kind of large-amplitude mode, i.e. the –OH···O= mode concerning proton tunneling between its two equivalent positions, is also involved. Remarks will be made, in the last Section 3, on the discrepancy of this G_{12} system from the G_6 system as well as on several other related systems that have been of current concern to the present author.

1. Theory

As implied in Introduction, this paper aims to modify a review article,[1] so that such as the above-mentioned experimental data can be (re)interpreted. Therefore, most of the expressions (notations/symbols in equations) are made to be consistent with theirs (the second last Chap. 15, especially its section 15.4.2 of NMn), except for a few cases. As stated in Introduction, the present theory is restricted to a molecular system that consists of a methyl group (top) and a planar parent group (frame), and that belongs to the G_{12} MSG. The only one exception is a planar 1:1 pair of MTrn and H_2O (MTrn$\cdot H_2O$), which belongs to G_6 MSG. Throughout this Section, one large-amplitude mode, i.e. only the torsional mode of the methyl group, is explicitly considered, thereby discounting another one, i.e. the –OH···O= stretching/tunneling mode of the proton in the last system(s).

1.1 Born–Oppenheimer-Type Approximation. First of all, the exact hamiltonian of the system (forgetting about such as nuclear spins) is partitioned in a form to satisfy the Eckart and Sayvetz conditions:[1]

$$H = H_0 + H', \tag{1a}$$

$$H_0 = H_e(\{q\};\ \{Q_v\},\ \rho) + H_v(\{Q_v\};\ \rho) + H_t(\rho) + H_R, \tag{1b}$$

$$H' = H_{\mathrm{nBO}} + V_{vt} + V_{vR} + V_{tR}. \tag{1c}$$

Here, subscripts (of H, i.e.) e, v, t, and R indicate the electronic, vibrational (other than torsional), torsional, and rotational parts/hamiltonians, respectively. While the variables $\{q\}$, $\{Q_v\}$ ($v = 1 - (3N - 7)$, N being the number of atoms in the molecule), and ρ designate the electronic, vibrational, and torsional coordinates, respectively. Though not explicitly indicated, their conjugate (angular) momenta are included in the corresponding hamiltonians (as operators before semicolon). The symbols of variables that are shown after semicolons are what should be considered as parameters in the implication of Born–Oppenheimer (BO)-type approximations. H_{nBO} is a non-BO (nBO) hamiltonian to cause breakdown of the genuine (adiabatic) BO (ABO) approximation. Three remaining V terms are similar nBO coupling terms with obvious meanings. If we disregard the last four terms, the zeroth-order eigenfunction is obtained as a variable-separated product,[1]

$$^{e,v,t,R}\Psi = {}^{e}\psi_e(\{q\};\ \{Q_v\},\ \rho)^{v}\Phi_v(\{Q_v\};\ \rho)^{t}\Phi_t(\rho)^{R}\Phi_R. \tag{2}$$

The superscripts at the left indicate adequate (set of) quantum numbers. This kind of wavefunction (Wf) may be used as a basis for the spectroscopy of the present system (disregarding the nBO terms; Section 15.3 of Ref. 1). Corresponding eigenvalues are dependent on the variables after the semicolon, and working as potential surfaces in the hamiltonian for the variables at lower levels. However, the observables are independent of the parameters, i.e. are those after integrating these. Throughout this paper, we ignore the Rotation, i.e. everything that contains the symbol R (Φ_R and parts of hamiltonian with R that depend on Euler angles, to say precisely).

1.2 Vibronic Coupling and Torsion–Vibration Coupling. In the case of VC (TEC and VEC; of toluene), Eq. 2 already contains most of the required information (in view of the H–T expansion on the crude BO (CBO) basis; except for the nBO contribution).[4] What should be examined was the nuclear-coordinate dependence of $\psi_e(\{q\};\ \{Q_v\},\ \rho)$.[4–6] Its F-S expansion on ρ was a novel feature, as proposed by the present author. In this paper, a morphing technique is introduced anew to describe the dependencies of both the electronic and vibrational Wf's on $\{Q_v\}$ and ρ at the same time, as was partially reported at a previous symposium:[6]

For the other two kinds of systems, the TVC term with the appearance of

$$^{0}V_{vt} = \sum_{n,v}({}^{\mathrm{c}}c_{n,v}Q_v \cos n\rho + {}^{\mathrm{s}}c_{n,v}Q_v \sin n\rho), \tag{3}$$

is considered, based on a further assumption that the symmetry coordinates, Q_v's (not normal coordinates, from now on), are independent of ρ. (This is different from the V_{vt} term in Eq. 1c as one of the nBO terms, just as the H–T VC term is different from the nBO term.) Within this formalism, vibrational-mode mixing, i.e. the interaction between the top and the frame, can be addressed mostly by this term with a variable, ρ. Furthermore, the torsional-coordinate dependence of the normal coordinate, which may have contributions from symmetry coordinates both in the frame and the top, could also be introduced with this term, again just like the case of VC, which is mostly described on the CBO basis. The deviation of the torsional motion from the free rotation can also be attributed to this term, at least partially. Though this is a mere extension/application of the conventional VC theory, little work on this stance appears to have been made, probably because most studies with MSG have been concerned with small mole-

cules, such as methanol (and NMn). Actually, in Ref. 1, only one section (15.4.3) concerning toluene is devoted to an introductory discussion of TEC. (This is the reason for the present author to be forced to accomplish a supplement before discussing the individual systems, including what should be published in the future, as Introduced.) The above Eq. 3 is nothing but an F-S expansion on ρ, with coefficients of either zero or proportional to Q_v, i.e. terminated at the first order. Thus, this term is introduced to expand the idea as developed for the VC, and can be taken as a modification of Eq. 15-3 in Ref. 1. (Actually, the cited equation, which is based on the T-S expansion, is not applicable to the internal rotation of the methyl group, though it might be applicable for describing such as the umbrella motion of ammonia, however, with required modifications.) Since it has to be totally symmetric on G_{12} MSG, the combination of the numbers n ($\approx K_i$; starting from 0 and terminated, e.g. at 6, for convenience) and (at most, $3N-7$) v are limited, as described below. Here, k_i ($=+/-|K_i|$) is the quantum number for the internal rotation, i.e. the torsion in the free-rotor limit (instead of t).[1] However, caution is required in choosing a totally symmetric linear combination for the degenerate vibrational mode, in contrast to the simple product for the non-degenerate mode. Three pairs of doubly degenerate (of e' symmetry only) vibrations are known for the present system, all restricted to those in the methyl group. These are numbered with the parameter r, following the review article.[1] (Do not confuse with the rotational quantum number, R.) Namely, they are three kinds of C–H vibrational modes (in the top: Table 15-5 and the notation in Eq. 15.64 of Ref. 1). Consulting the reducing relationship of $e' \times e' = a_1' + a_2' + e'$, the corresponding (totally symmetric) TVC term (of the a_1' symmetry) is confirmed to have the appearance of

$$ {}^{12}V_{vt}{}^{r} \propto S_{ra}\cos 2\rho - S_{rb}\sin 2\rho, \tag{4a} $$

$$ \propto S_r{}^{+}\exp(2i\rho) + S_r{}^{-}\exp(-2i\rho). \tag{4b} $$

Here, symmetry coordinates, $S_r{}^{+}$ and $S_r{}^{-}$, with complex expansion coefficients are taken to be inverse transformations of

$$ S_r{}^{\pm} = 2^{-1/2}(S_{ra} \pm iS_{rb}), \tag{5a} $$

with, e.g. for the case of asymmetric CH stretching vibrations in the methyl group,

$$ S_{r'}{}^{+} \equiv 3^{-1/2}\{\Delta r_1 + \Delta r_2\exp(\pm(2\pi/3)i) + \Delta r_3\exp(\pm(4\pi/3)i)\}\exp(\pm i\phi), \tag{5b} $$

($r' = 10$ in case of NMn: The precise (local) coordinates $\{r_j;\ j = 1\text{–}3\}$ in this formula are defined in Fig. 15-6 of Ref. 1.). Though not essential, the term $\exp(\pm i\phi)$ with an arbitrary phase factor, ϕ, is attached so that the equivalence of three protons is guaranteed. Furthermore, if ϕ is set to be either 0 or $\pi/2$, their real and imaginary parts are correlated with either S_{ra} or S_{rb}, respectively (Table 15-5 of Ref. 1; for the staggered and eclipsed conformations, vide infra). The advantage of the present pair of symmetry coordinates, $S_r{}^{\pm}$ over $S_{ra/b}$, is evident not merely in the appearance to honor the symmetry/permutation operation of C_3 in the methyl group, but rather in the fact that the former can be naturally transformed into another form to define another pair of variables, $\{\Delta r, \alpha\}$:

$$ S_{r'}{}^{\pm} = \Delta r\exp(\pm i\alpha), \tag{5c} $$

so that the vibrational angular momentum corresponding to the operator conjugate to α is sustained. (A general discussion on the vibrational angular momentum, for the two-dimensional isotropic harmonic oscillator, is given in section 11.3.2 of Ref. 1.) Now, the explicit signs ($\pm$) in the apparently equivalent equations are understood to indicate the sense of rotation. Actually, the definition

$$ \Delta r = 3^{-1/2}(\Delta r_1{}^2 + \Delta r_2{}^2 + \Delta r_3{}^2)^{1/2}, \tag{5d} $$

can easily be discerned by comparing the absolute squares of Eqs. 5b and 5c. However, a formal expression of α can be obtained just by comparing the real and imaginary parts of Eqs. 5b and 5c with a little more complex appearance, as defined by the equality

$$ \begin{aligned}(\Delta r)^2\cos 2\alpha = {} & (\Delta r_1\cos\phi + \Delta r_2\cos(\phi + 2\pi/3) \\ & + \Delta r_3\cos(\phi + 4\pi/3))^2 \\ & - (\Delta r_1\sin\phi + \Delta r_2\sin(\phi + 2\pi/3) \\ & + \Delta r_3\sin(\phi + 4\pi/3))^2.\end{aligned} \tag{5e} $$

By simple trigonometry, the right-hand side of this equation is shown to be a mere function of 2ϕ (twice of the arbitrary phase factor). Therefore, a one-to-one correspondence between α and ϕ is noted. Thus, as a final formula of TVC, the proportionality

$$ {}^{12}V_{vt}{}^{r} \propto \Delta r\exp(i(\alpha + 2\rho)) + \Delta r\exp(-i(\alpha + 2\rho)) \quad (\propto \Delta r\cos(\alpha + 2\rho)), \tag{4c} $$

is obtained. In correspondence to this kind of symmetry coordinates, their degenerate vibrational levels could be distinguished more adequately with the sign ($\pm$) of the vibrational angular momentum, ℓ (of such as $+1$ or -1), just like the case of the torsional levels (in the free-rotor limit) with corresponding angular momenta. In this paper, restrictions are made with $|\ell| = 0,\ 1$ and accordingly with $v_r = 0,\ 1$, higher vibrational levels not being considered. (More comprehensive discussion of this subject, i.e. the interaction between two kinds of local angular momenta, including the case of $|\ell| > 1$, is set aside for future study.) For example, we can now define a sort of torvibrational (an analogy to the terminology of vibronic) levels with the symbol $\langle v_r\ell, k_i\rangle$, where each digit (non-natural integer) is obviously concerned with one of the two kinds of variables/operators in Eq. 4c, respectively (representing such as $|0, \ldots, 0;\ v_r\ell, k_i;\ 0\rangle$). This symbol of angle brackets is reserved for representing the possible scheme of TVC by Eq. 4c, with the selection rule characterized by the four kinds of combinations of $\Delta v_r = \pm 1$ and $\Delta k_i = 2\Delta\ell = \pm 2$, i.e. of $\Delta(v_r\ell) = \pm 1$ and $\Delta k_i = \pm 2$, as will be described below. In this way, the TVC with this Eq. 4c is recognized to involve the exchange of angular momentum between the particular vibration and the torsion within the top. Thenceforth, with the above set of equations, a supplement to the current theory of MSG was produced.

1.3 Approximate Wf's. A discussion will now be made in accordance with the procedure of the BO-type approximation. This is somewhat in parallel with a presentation in a review article (Chap. 15 of Ref. 1).

1.3.1 Electronic Wf: The first is concerned with the VC (TEC), mostly described with the nuclear-coordinate dependency of $\psi_e(\{q\};\ \{Q_v\},\ \rho)$. Since an introductory discussion is already made in Ref. 4, its Eq. 6 for the ABO Wf of the S_1 state (in toluene) only is reproduced as

$$\begin{aligned}\psi_1(\{q\},\ \rho) &= (1/2)^{\mathrm{e}}\psi_1{}^0(\{q\};\ \{Q_v(\rho)\},\ \rho)(1+\cos 6\rho)\\ &+ (1/2)^{\mathrm{s}}\psi_1{}^0(\{q\};\ \{Q_v(\rho)\},\ \rho)(1-\cos 6\rho)\\ &+ (2/3\pi)\int_0^{2\pi}\langle{}^{\mathrm{e}}\psi_2{}^0(\{q\};\ \{Q_v(\rho)\},\ \rho)|\psi_1(q,\rho)\rangle\cos 3\rho\mathrm{d}\rho\\ &\times {}^{\mathrm{e}}\psi_2{}^0(\{q\};\ \{Q_v(\rho)\},\ \rho)(1+\cos 6\rho)\cos 3\rho\\ &+ (2/\pi)\int_0^{2\pi}\langle{}^{\mathrm{s}}\psi_2{}^0(\{q\};\ \{Q_v(\rho)\},\ \rho)|\psi_1(q,\rho)\rangle\cos 3\rho\mathrm{d}\rho\\ &\times {}^{\mathrm{s}}\psi_2{}^0(\{q\};\ \{Q_v(\rho)\},\ \rho)(1-\cos 6\rho)\cos 3\rho, \qquad (6a)\end{aligned}$$

with revisions by such as

$$Q_v(\rho) = {}^{\mathrm{e}}Q_v\cos^2 3\rho + {}^{\mathrm{s}}Q_v\sin^2 3\rho. \qquad (6b)$$

In this expression, not only the coefficients of Wf's, but also the nuclear coordinates (other than the torsional coordinate, ρ), are subject to the F-S expansion on ρ. Namely, Eq. 6b indicates nothing but the morphing procedure with terminals at two sets of ρ's, i.e. two sets of coordinates corresponding to the two kinds of extreme structures with the C_s symmetry of the molecular point group (MPG), i.e. eclipsed (the symmetry plane being coincident with the molecular plane, frame) and staggered (the symmetry plane being vertical to the frame) conformations. The superscripts at the left, i.e. e and s on the CBO Wf's and the coordinate Q_v indicate these conformations. A more detailed discussion will be made in the section 2.1 concerning Toluene, while applying this equation for the derivation of the revised version of Eq. 9 in Ref. 4.

1.3.2 Vibrational Wf: As for the vibrational Wf (to be determined following electronic Wf), (possible) degenerate (e') modes only are considered (to emphasize the importance of the present supplement). If the symmetry coordinates for these are all assumed to be independent of ρ, as was applied to derive Eq. 3, they are given in Table 15-5 of Ref. 1, as was already described with $\{S_{ra}, S_{rb}\}$. However, other choices are also possible, e.g. by its Eq. 15-64, i.e. $\{\cos\rho\ S_{ra} - \sin\rho\ S_{rb}, \sin\rho\ S_{ra} + \cos\rho\ S_{rb}\}$ which may be taken/defined as a transformation of $\{S_{ra}, S_{rb}\}$ with $[\cos\rho, \sin\rho]$. (An expression like this, i.e. a pair of functions in a square bracket as an operator on a pair of the variables in a brace to create another pair is to be used later on.) With this kind of procedure, the TVC term of Eq. 3 on the CBO-type approximation is partially eliminated while being incorporated into the ρ-dependence of the normal coordinate in conformity with the ABO-type approximation. This is correspondent to a modification of Eq. 5b by replacing ϕ with ρ. Then, the vibrational levels of the modes with the e' symmetry are automatically split into a_1'' and a_2'' levels, in accordance with the scheme of reduction: $e' \times e'' = a_1'' + a_2'' + e''$. It has to be noted, however, that this scheme represents by no means the "true/conceptual" TVC to destroy the BO-type approximation, as was assumed for the derivation of Eq. 2. Actually, a_1'' and a_2'' symmetries are assigned just to the modified vibrational Wf's, as prepared from the pair of vibrational Wf's of the e' symmetry into forms with the dependence on ρ. However, the remaining/third e'' term is apparently redundant, though it might appear to represent a pair of concerted motions of vibration and torsion. This is actually useless with no experimental fact to be described by this pair of Wf's. Since the frequencies of the two kinds of modes are quite different from each other, their combined waveforms look like a pair of FM signals. Thus, the last e'' term in the expansion may be regarded as symbolically reserved for the torsional level, kept degenerate with no TVC term to split them. These nondegenerate/reduced/split symmetry coordinates have been believed to be most adequate to couple/mix with those in the frame (with a C_{2v} symmetry of MPG) and have been approved in the literature.[1,10,11] However, an alternative transformation of $\{S_{ra}, S_{rb}\}$ with $[\cos 3\rho, \sin 3\rho]$ is strongly recommended in this paper, as was picked up from many other possible pairs of functions that are dependent on ρ with various symmetry species (not restricted to either e' or e''), e.g. including the totally-symmetric (a_1') pair of $(1 \pm \cos 6\rho)$, the only condition being orthonormality (vide infra). (Actually, Papoušek et al.[11] happened to use $[\cos 2\rho, \sin 2\rho]$, in spite of their inconsistent assignments of the split pair with $a_1'' + a_2''$.) The reasons are: (1) The vibrational modes modulated with $(\cos 3\rho, \sin 3\rho)$ may follow the torsional motion most faithfully, in resemblance to the case of the electronic Wf of Eq. 6 and in accordance with the concept of A-O following nuclei or of morphing. (2) If either a staggered or eclipsed conformation is at the potential minimum, these are assessed to be the best set of symmetry coordinates (to describe the ground vibrational level). (3) The pair of functions, $(\cos 3\rho, \sin 3\rho)$, may be regarded to be degenerate as of the e'' symmetry, while representing the pair of torsional levels in the free-rotor limit (e.g., at the (high) vibrational level, 10_1). At present, we have little experimental data to distinguish these alternative possibilities except for the broadness of the bands to favor TVC, as Introduced. Apart from the availability of the experimental data, this problem can be regarded as a matter of the choice of the basis sets (for the fast convergence towards the description of the spectroscopical observation, as are encountered in many fields of spectroscopy, e.g. in classifying Hund's Case (a), (b), and so on). Irrespective of the choices, the coupling involving these modes is judged to be stronger than that in the other modes, as can be confirmed by examining the coupling matrix elements and the ρ-dependency of the normal coordinates, to be described later (subsection 2.1.1).

Now, as a new approach, a discussion will be made based on the simplest possible model to mimic Eq. 2, i.e. of ρ-independent vibrational modes of such as Eqs. 5a–e, so that Eqs. 3 and 4 for TVC are just applied to attain the true Eq. 2. With Eq. 4c and the notation of the torvibrational level, $\langle v_r \ell, k_i\rangle$ defined previously, the $\langle +1, k_i\rangle - \langle 0, k_i \pm 2\rangle - \langle -1, k_i\rangle$ schemes are available to cause a splitting of a degenerate (set of) $\langle \pm 1(e'), k_i\rangle$ levels into (sets of) their linear combinations at the zeroth order, with little restriction on k_i in spite of the explicit 2ρ dependence in Eq. 4c. At this stage, we encounter the problem of the choices in the transformation, as occurred while deriving the nondegenerate symmetry coordinates in the last paragraph, now in that of $\{|+1\rangle, |-1\rangle\}$ (not of $\{|1_a\rangle, |1_b\rangle\}$) with either $[\exp(i\rho), \exp(-i\rho)]$ or $[\exp(3i\rho), \exp(-3i\rho)]$, (irre-

spective of the symmetry species of the concerned k_i level). To say precisely, we can not completely exclude any other transformation with $[\exp(in\rho), \exp(-in\rho)]$ $(n \neq 0)$ as well as a pair of the exponential functions whose arguments are $\pm$ of a pure imaginary number independent of ρ, e.g. $\exp(\pm 2\pi i) = 1$ corresponding to the creation of $|1_{a/b}\rangle = 2^{-2}(|+1\rangle \pm |-1\rangle)$ which should not be degenerate any longer (so the parameter ϕ could be adjusted, e.g. at $\rho + \pi/2$). Of course, the author's choice is with $[\exp(3i\rho), \exp(-3i\rho)]$ based on the concept of morphing. Regardless of the above two alternative choices (with the dependencies on ρ or 3ρ), the set of $\langle 1(a_1''), k_i\rangle$ and $\langle 1(a_2''), k_i\rangle$ levels are obtained. These are the same as would be attained from the set of $\{|1_a\rangle, |1_b\rangle\}$, transformed with $[\cos 3\rho, \sin 3\rho]$, as described in the last paragraph. Here, the symmetry species, as indicated in the parentheses, are concerned only with the vibrational mode, $v_r\ell$, irrespective of the symmetry species for the torsional levels, k_i's, and can be confirmed by drawing/imaging the shapes of the Wf's, while consulting the character table of G_{12} (Table A-24 of Ref. 1). This can be done without invoking the relationship of such as $e' \times e'' = a_1'' + a_2'' + e''$, in contrast to the case of the ordinary TVC to mix the products of the vibrational and torsional Wf's of common symmetry species with any term in Eq. 3. As long as the k_i's are fair quantum numbers (as in the Table 1 to be described below), the available scheme with k_i has a precise equivalence to that which is restricted based on the exact symmetry species. This was confirmed by the author for smaller K_i values of less than 7, at least for Eq. 4c. This splitting of the e' level into the a_1'' and a_2'' levels apparently corresponds to what was described in the last paragraph. However, in the present description, mixing among various levels with different k_i is also predicted as higher order contributions, with the selection rule of $\Delta k_i = \pm 2$ for further mixing by Eq. 4c.

Table 1. Species of Torsional Wf's of Molecules with Methyl Groups in the MSG G_{12}/G_6, with Reference to the Two Kinds of Torsional Quantum Numbers, v_t and k_i

v_t	k_i	$\Gamma(G_6)$	$\Gamma(G_{12})$	$\Gamma(G_{12})\times a_1''$
0	0	a_1	a_1'	a_1''
	±1	e	e''	e'
1	+2/−2	e	a_1'/a_2' (e')	a_1''/a_2'' (e'')
	−3	a_2	a_2''	a_2'
2	+3	a_1	a_1''	a_1'
	±4	e	e'	e''
3	±5	e	e''	e'
	−6	a_2	a_2'	a_2''
4	+6	a_1	a_1'	a_1''
	±7	e	e''	e'

The peculiarity in the line of +2/−2 should be noted, of which detailed interpretation is made in the text.

1.3.3 Torsional Wf: As for the symmetry species (Γ) of torsional Wf's to be determined at the last step of the BO-type approximation (in this paper), a correlation table with k_i (the torsional quantum number in the free-rotor limit) is available in the literature (e.g., Table 15-3 of Ref. 1). However, it is due to neglecting the TVC. If the degeneracy of the e' vibrational levels (of such as an asymmetric pair of the CH stretching vibrations in the top) happened to be practically retained, even after the trial TVC (between vibrational levels, e.g. corresponding to the scheme $e' \times e'' = a_1'' + a_2'' + e''$, as described above), with the possible splitting being not so significant compared to either (1) the variation of its energy (frequency) with ρ or (2) the torsional energy (frequency) itself, then the coupling scheme of $\langle 0, +2\rangle - \langle \pm 1, 0\rangle - \langle 0, -2\rangle$ between torsional levels with the Eq. 4c emerges as a predominant scheme in accordance with the reduction of $e' \times e' = a_1' + a_2' + e'$, to be evaluated firstly before the above coupling scheme for the torsional levels, corresponding to one of the choices of the basis sets. (In analogy with the case in subsection 2.3.2, the last e' term could be regarded as being reserved for the vibrational level, this time, not being subject to the true TVC term V_{vt}, for no more combination of the torsional levels with e' symmetry is available to demand the selection rule of $\Delta k_i = \pm 2$.) This second-order scheme is nothing but the off-diagonal term between degenerate $\langle 0, \pm 2\rangle$ levels to split them into levels whose (torsional) Wf's are $\pi^{-1/2}$ times of $\cos 2\rho$ (a_1') and $\sin 2\rho$ (a_2'), respectively. (This splitting of e' into a_1' and a_2' species with the transformation [1, 1], being independent of ρ with no other choice, is in contrast to the case of the e' vibrational modes, whose splitting was assessed to be into those of a_1'' and a_2'' symmetries.) Table 1, containing a line of +2/−2, was made to comprise this fact, as a supplement/correction to/of Table 15-3 of Ref. 1. Also indicated in the table is their correlation with the quantum number (v_t) of the torsional motion in the hindered-rotor limit. (The assumption of a hindered-rotor limit is adequate for levels well below the potential barrier for "torsion". Corresponding to this arrangement, their energies should increase while going down this column.) Besides $\Gamma(G_{12})$ (species for the G_{12}), $\Gamma(G_6)$ is also listed in this table (no splitting of the e levels by the TVC being assumed, as will be Remarked). This is for later comparison between the two kinds of MTrn's.

The general theoretical discussion is over, while describing new features of MSG, as based on an F-S expansion of the coupling coefficients. Exploitation of the above knowledge will be made for interpreting the actual spectroscopical data, as will be presented in the next Section.

2. Application

The above theory is now applied to real systems. This Section is divided into three sections, titled with the names of the molecules. Therefore, within each section, an account of the experimental data as well as their interpretation is made.

2.1 Toluene. An introduction to this section was already made in Ref. 4, and in the above Sections. In short, a strict proof of the intensity-borrowing mechanism with the torsional mode is the target. Therefore, the role of this section is reduced to show that the presumed TEC (mixing) coefficient,

$$^{s/e}C \equiv \int_0^{2\pi} \langle ^{s/e}\psi_2{}^0(q;\ \rho)|\psi_1(q,\rho)\rangle \cos 3\rho \mathrm{d}\rho/\pi, \qquad (7)$$

in Eq. 6a does not cancel, i.e. to make a more detailed derivation of its Eq. 9 (i.e., of the required overlap integral in this formula) from the present Eq. 6. First of all, the concerned overlap integral is reproduced with modifications and corrections:

$$^{s/e}S(\rho) \equiv \langle ^{s/e}\psi_2{}^0(\{q\};\ \rho)|\psi_1(\{q\},\ \rho)\rangle, \qquad (8a)$$

$$\approx \langle ^{s/e}\psi_2{}^0(\{q\})|^{e/s}\psi_1{}^0(\{q\})\rangle(1 \pm \cos 6\rho), \qquad (8b)$$

$$\propto \Sigma c_{ij}\langle ^{s/e}\pi_i{}^*|^{e/s}\pi_j{}^*\rangle(1 \pm \cos 6\rho), \qquad (8c)$$

$$\propto \Sigma c^{kl}\langle ^{s/e}(1s)_H{}^k|^{e/s}(1s)_H{}^l\rangle(1 \pm \cos 6\rho). \qquad (8d)$$

Before deriving the above equations, let's examine what kind of information we can acquire from the current ab initio calculation, e.g. with the GAUSSIAN 94 program, not restricted to optimization of the geometry.[18,19] Firstly, LCAO MO's are obtained by an algorithm based on the Hartree–Fock–Roothaan approximation for any geometries. With this set of MO's, the electronic Wf's as eigenfunctions of $H_e(\{q\};\ \{Q_v\},\ \rho)$ in Eq. 1b are calculated in terms of the Slater determinants. This is exactly what we call CBO Wf's (vide supra).[4,5] However, what are required are ABO Wf's as analytical functions of the nuclear coordinates, $\{Q_v\}$ and ρ. This is the reason why we introduce the AO-following-nuclei approximation as well as the morphing technique. Thus, the simplest possible ABO Wf is obtained as Eq. 6, i.e. an analytical function of the only one variable of ρ. However, this still has a quite complex dependence on ρ, as may be recognized from Eq. 6b. Also to be noted is the fact that the parameter, $^{s/e}S(\rho)$, itself is contained in its definition, as can be discerned by the direct multiplication of Eq. 6a (from the left) with $^{s/e}\psi_2{}^0(\{q\};\ \{Q_v(\rho)\},\ \rho)$, followed by integration over $\{q\}$. Actually, they can be formally evaluated by solving simultaneous integral equations in a self-consistent manner (by the computer):

$$\begin{aligned}
^{s/e}S(\rho) = (1/2)&\langle ^{s/e}\psi_2{}^0(\{q\};\ \{Q_v(\rho)\},\ \rho)| \\
&{}^{e/s}\psi_1{}^0(\{q\};\ \{Q_v(\rho)\},\ \rho)\rangle(1 \pm \cos 6\rho) \\
&+ (2/3\pi)\int_0^{2\pi} {}^eS(\rho)\cos 3\rho \mathrm{d}\rho \\
&\times \langle ^s\psi_2{}^0(\{q\};\ \{Q_v(\rho)\},\ \rho)| \\
&{}^e\psi_2{}^0(\{q\};\ \{Q_v(\rho)\},\ \rho)\rangle(1 + \cos 6\rho)\cos 3\rho \\
&+ (2/\pi)\int_0^{2\pi} {}^sS(\rho)\cos 3\rho \mathrm{d}\rho \\
&\times \langle ^e\psi_2{}^0(\{q\};\ \{Q_v(\rho)\},\ \rho)| \\
&{}^s\psi_2{}^0(\{q\};\ \{Q_v(\rho)\},\ \rho)\rangle(1 - \cos 6\rho)\cos 3\rho. \qquad (9)
\end{aligned}$$

Just by inspection of this pair of equations, we can assert that a trivial solution of the type

$$^{s/e}C = \int_0^{2\pi} {}^{s/e}S(\rho)\cos 3\rho \mathrm{d}\rho/\pi = 0, \qquad (10)$$

does not exist. Thus, the above type of TEC is proved to be an existent scheme for intensity borrowing.

The proof of the TEC scheme is over as above. However, from the view point of the spectroscopist, any other practical procedure to estimate this parameter is desired, so that such as a deuterium isotope effect could be interpreted.[4] Actually, this kind of approach was already taken for the case of the usual VC, e.g. in pyrazine.[5] Accordingly, the set of Eqs. 8a–d may be regarded as a symbolical representation of this concept.

One more job being left to be done prior to the derivation of Eqs. 8a–d is to explore how strong is the TEC. For that purpose, the theoretical calculation by Kroemer et al.[16] is most useful, as already described in Ref. 4. What should be cited here is their Fig. 3, i.e. the result of a computer experiment on the orientation of the transition moment as a function of ρ: (1) The orientation was within the molecular plane regardless of ρ. (2) For the staggered conformation, it was parallel with the b axis. This corresponds to the pure L_b transition. (3) The maximum deviation from the b axis was observed to be 32° at the eclipsed conformation. This means that the contribution of the L_a band to the total intensity (by TEC) is $\sin^2 32^\circ = 0.28$, at this particular conformation. From this observation, we can make a semi-quantitative estimation of the mixing coefficient, $^{s/e}C$, to be less than $\sin 32^\circ (f(L_b)/f(L_a))^{1/2} \sim 0.06$, the symbol f indicating the pure oscillator strength of the corresponding transition.

Encouraged with the above conclusion concerning Eq. 9 and noting that $^{s/e}C$ (related to $^{s/e}S(\rho)$) is smaller than 1 at more than one order of magnitude, we'll neglect the higher order terms in it (vide supra, including Eq. 9). Then, the first near equality of Eq. 8b is immediately derived. Thus, what has to be evaluated first is the overlap integral between two kinds of CBO Wf's different in both electronic states (S_1 vs S_2) and conformations (e vs s). Regardless of the actual shapes of CBO Wf's as linear combinations of Slater determinants, the overlap integral has contributions mostly from those between electronic configurations with common MO's, except for one at most. Otherwise, they should be nearly cancelled in spite of the difference in geometries, for the π-type MO's are distributed mainly in the aromatic ring. Since we are concerned with the S_1 and S_2 states, the integral is reduced to a linear combination of overlap integrals between several pairs of different LUMO's, leading to the first proportionality of Eq. 8c. The last proportionality of Eq. 8d is based on the assumption that the MO coefficients on the benzene ring should not be significantly dependent on ρ at the zeroth order (before TEC), so that the overlap integral between the LUMO's is cancelled for the area within the ring. Therefore, hyperconjugation involving such as 1s (2s) orbitals of the hydrogen atoms in the methyl group is presumed to play a major role. The derivation is over, all of the Eqs. 8a–d. However, this kind of discussion cannot be made any more until more detailed experimental data become available, such as the combination bands between the vibration and torsion, and a quantitative comparison between d_0 and d_3, as already mentioned in Ref. 4, not restricted to the case of toluene (the next Section 4).[4–6,8,16,17]

2.2 Nitromethane. This section consists of two subsections. The first is for a theoretical prediction of "ρ-dependent" normal coordinates and their frequencies with a GAUSSIAN 98 suit of programs, at the level of MP2/6-31G(d, p).[18] The second is devoted to a description of concerned experimental

Table 2. Normal Coordinates of Nitromethane at Staggered ($\rho = \pi/6$; Left) and Eclipsed ($\rho = 0$; Right) Conformations

#	Character	G_{12}	$C_s(b)$	calcd	obsd[a)]	calcd	$C_s(c)$	G_{12}	Character
1	S_1	a_1'	a'	3171	2974	3172	a'	a_1'	S_1
2	S_5			1461	1397	1460	(in plane)		S_5
3	S_3 (, S_2)			1436	1380	1435			S_3 (, S_2)
4	S_2, S_3, S_5			944	918	944			S_2, S_3, S_5
5	S_4, S_5 (, S_3)			672	657	668			S_4, S_5 (, S_3)
6	S_{10b}	a_1''	a''	3312	3080	3311	a'	a_1''	S_{10a}
7	S_6 (, S_7)	(in plane)		1815	1583	1814	(in plane)		S_6 (, S_7)
8	S_{11a}			1530	1434	1530			S_{11b}
9	S_{12b}			1149	1131	1147			S_{12a}
10	S_7, S_{12b} (, S_6)			483	475	480			S_7, S_{12a} (, S_6)
11	S_{10a}	a_2''	a'	3287	3045	3289	a''	a_2''	S_{10b}
12	S_{11b}	(o. o. plane)		1537	1410	1537	(o. o. plane)		S_{11a}
13	S_{12a}			1168	1096	1165			S_{12b}
14	S_9, S_{12a}			600	603	607			S_9, S_{12b}
—	torsion	—	a''	40	—	$50i$	a''	—	torsion

a) Taken from Table 2 of Ref. 12 as summarized by Gorse et al., but with one interchange in the assignments.

data and their interpretation, as Introduced.

2.2.1 Normal Coordinates as Dependent on the Torsional Coordinate, ρ: These were numerically obtained in two steps: (1) Determination of the reaction path from the saddle point of the eclipsed structure to the potential minimum of the staggered conformation (as may be parameterized with a classical variable, ρ). (2) Calculation of the (ρ-dependent) normal coordinates and their frequencies at the conformations through the path. It has to be noted that the second step is based on the harmonic approximation, except for that of the reaction coordinate. Namely, the calculated result on the torsional mode is not exactly correspondent either to that in Eq. 2, as based on the BO-type approximation, or to that in Eq. 3, as assumed to be independent of ρ. The results on only the two extreme structures are shown in Table 2, along with symmetry assignments on the pairs of MPG(s) and MSG. The mode numbers (#) are coincident with those in Table 8 of Ref. 12. The symbols of symmetry coordinates, including symmetry axes in the description of "character", should be referred to those in Table 15-5 of Ref. 1. An exact one-to-one correspondence is evident in both the characteristics and frequencies with some dependencies on ρ, manifesting the difference of the symmetry properties of MPGs. The most notable is an interchange of the subscripts $a \leftrightarrow b$ (of the modes originate from the degenerate e' symmetry coordinates), corresponding to the interchange in the symmetry planes ($\sigma_h(b)$ and $\sigma_h(c)$ as based on the convention in Ref. 1). These assessments were further confirmed by examining the ρ dependence of the energies through the path (e.g., for 0°, 7.7°, 15.3°, 22.8°, and 30°) with no evidence of any cross-over, other than avoided crossing involving an interchange of subscripts a and b. All of the small ρ dependency could be interpreted as sinusoidal with the argument of 6ρ and/or 3ρ, corresponding to the theoretical discussion in subsection 1.3.2. The most noteworthy 3ρ dependence was observed for a pair of modes, 6 and 11, which could be described mainly as a transformation of $\{S_{10a}, S_{10b}\}$ with $[\cos 3\rho, \sin 3\rho]$. (In view of the morphing, there is no reason to support the expansion with $[\cos \rho, \sin \rho]$, as in the conventional **FG** matrix treatments.[1,10,11]

The above pair and the other two kinds of pairs represent the split levels with the scheme $e' \times e'' = a_1'' + a_2'' + e''$, as described in subsection 1.3.2. Thus, a transformation with $[\cos 3\rho, \sin 3\rho]$ is recognized to be the best choice in view of the fast convergence. Contrary to this, the pair of such as $\{S_{10a}, S_{10b}\}$ may be the worst choice accompanied by a cross over of the energy levels with a variation of ρ. However, Eq. 5b may be regarded to be the most conservative pair to retain the degeneracy at the best, with the smallest splitting of the energies at the zeroth order.

Finally, a comment should be made concerning the "frequencies" of the torsional mode, such as given in the Table 2. These values have little to do with the torsional Wf, ${}^t\Phi_t(\rho)$, as defined in Eq. 2. For these are merely reflecting the (square-root of the) curvature on the reaction coordinate (at the two ends).[19] Actually, at this level of calculation, the difference in the potential energies between the two conformers, i.e. the potential barrier for the internal rotation, was determined to be $\sim$8 cm^{-1} ($\sim$4-times larger than the experimentally presumed value;[13] the next subsection), much less than the calculated frequency, 40 cm^{-1}. Similar, but a little more complex, results were obtained for *N*-methylpyrrole (NMP), to be Remarked later.[20,21]

2.2.2 IR Spectrum of Nitromethane: Firstly, the IR spectrum of NMn reported by Jones and Sheppard[9] is examined, restricted to the possible e' modes. After struggling with their own data, they accomplished assignments. Their result in the Q-branch areas corresponding to the transitions with $|\Delta k_i| = 1$ may be represented as follows, with a slight modification of their Eq. 12 (/cm^{-1}):

$$\nu_9[\upsilon_a(CH_3)]; \quad \nu = 3083.3 \pm 6.5 \pm 7.688|k_1| + 0.052{k_1}^2, \quad (11a)$$

$$\nu_{10}[\delta_a(CH_3)]; \quad \nu = 1445.4 \pm 2.4 \pm 10.682|k_1| + 0.030{k_1}^2, \quad (11b)$$

$$\nu_{11}[r(CH_3)]; \quad \nu \approx 1118 \pm 27 + f(k_1;\ ?). \quad (11c)$$

(The mode number (9) is different from that (10) defined in Ref. 1, as was cited in the Eq. 5, corresponding to that (10) in the present Table 2.) While making these assignments, no transition with such as $\Delta k_i = \pm 4$ and its combination with $\Delta k_i = 0,\ \pm 1$ was identified, as would correspond to the coupling/mixing schemes of such as $\langle +1, k_i + 2\rangle - \langle 0, k_i\rangle - \langle +1, k_i - 2\rangle$, $\langle +1, k_i\rangle - < 0, k_i \pm 2\rangle - \langle -1, k_i \pm 4\rangle$ and others, as predicted in the last Section. Even if they had any contribution in spectra, no corresponding peak could be observed, possibly because it would be buried in the observed broad band. Therefore, to clarify this possibility, spectra at both higher resolution and lower temperature are desired. Since the extent of splitting (13, 4.8, and 55 cm^{-1}) is comparable to, or larger than, the height of the potential barrier of the torsional motion ($\sim$2 cm^{-1} for the 0 (ground vibrational) level[13]), we may safely judge that the e' vibrational levels are practically split into pairs of $\{a_1'', a_2''\}$ levels, in conformity to the theoretical prediction in the last subsection. This can be easily interpreted based on the above two theories. Either the present theory of TVC (with $n = 3$) or the previous theoretical assessments based on the **FG** matrix treatment (with $n = 1$ or 3 ?).[10,11] The latter appears to be equivalent to dismiss the BO-type approximation of Eq. 2, the kinetic energy involving ρ being incorporated at least partially.[10,11] Also, no splitting of the torsional level with $K_i = 2$ (e') is evident in the observed microwave spectra,[13] in accordance with the theoretical prediction in the last Section. In conclusion, we cannot absolutely decide which scheme, i.e. either the conventional one or that based on the present theory of TVC, is better to describe the vibrational levels in NMn, though the broadness of the band would favor the latter. Thus again, the IR spectra at higher resolution and at lower temperature (by any means) are desired!

2.3.5 Methyltropolone's. This section is concerned with an interpretation of the electronic spectra, i.e. the fluorescence (excitation) spectra of MTrn and MTrn·H_2O observed by Nishi et al.[14,15] As already mentioned, MTrn is quite different from the above two molecules in that it contains another kind of large-amplitude mode of proton tunneling, i.e. its –OH···O= mode. However, its electronic spectra have a similarity to those of MTrn·H_2O, which is the G_6 system with only one large-amplitude mode of internal rotation. This is because, in the latter system, the potential minimum of the location of the proton in the intramolecular hydrogen bond is restricted only at one site.[15] The most significant peculiarity in these systems is an apparent splitting of the $2E$ levels (only, labeled corresponding to the $K_i = 2$ levels with the e symmetry for the G_6 MSG of MTrn·H_2O) in the S_1 state of MTrn,[15] no corresponding splitting being observed in MTrn·H_2O.

To interpret these facts in an acceptable form, we'll separate the hamiltonian of MTrn as

$$H = H_L(x + x_0) + H_R(x - x_0) + V_C, \quad (12)$$

with a form different from that of Eqs. 1a–c. Here, x, x_0, and $-x_0$ indicate the coordinates of the hydrogen-bonded proton, and its potential minima at the right- (// $\rho = 0$) and left-hand (// $\rho = \pi$) sides, respectively. With these variables, both H_L and H_R are defined as hamiltonians to approximate the true hamiltonian, H, most faithfully near $x = -x_0$ and x_0, respectively. They represent the geometries belonging to the C_s MPG. (In other words, H_L and H_R are defined to be zero near $x = x_0$ and $-x_0$, respectively. For actual evaluations of the Wf's and energies, any strict mathematical expression may be made, appealing either to projection operators or to the morphing technique as an elegant expression.) Therefore, by taking account of the permutation symmetry of the three protons, these hamiltonians are judged to belong to the G_6 MSG. The last V_C term represents the residual portion. Thence, the hamiltonian, H, as a whole, is sustained to belong to G_{12} MSG. Accordingly,

$$\begin{aligned} {}^{e,v,t}\Psi_\pm = 2^{-1/2}\{&{}^e\psi_e(\{q\};\ \{Q_v\}',\ x - x_0,\ \rho) \\ &\times {}^v\Phi_v(\{Q_v\}',\ x - x_0;\ \rho)^t\Phi_t(\rho) \\ &\pm {}^e\psi_e(\{q\};\ \{Q_v\}',\ x + x_0,\ \rho) \\ &\times {}^v\Phi_v(\{Q_v\}',\ x + x_0;\ \rho)^t\Phi_t(\rho + \pi)\}, \end{aligned} \quad (13)$$

is derived as an approximate eigenfunction, where $\{Q_v\} \equiv \{\{Q_v\}',\ x\}$. This is nothing but a linear combination of the eigenfunction for the approximate hamiltonian (belonging to the MSG of G_6). Thus, the BO-type approximations are no longer applied. Group-theoretical reasoning for this breakdown can be made using the TVC term with the simplest possible form of

$${}^{12}V_{vt}{}^x \propto x\cos 3\rho, \quad (14)$$

the symmetry species of x being a_1''. This term is already introduced by Sanders[22] to describe a similar system, 3-hydroxy-2-methylacrylaldehyde (or 3-hydroxymethacrylaldehyde; HMA: a tautomer of methylmalonaldehyde), i.e. another G_{12} system with intramolecular hydrogen bonding. If we consider the states with excitation in the torsional mode only, i.e. with $e = 0/1$ (S_1 and S_0) and $v = 0$ (except for the tunnel splitting for the mode x), the above functions can be simplified further. Namely, for both ${}^{0/1}\psi_e$ and ${}^0\Phi_v/{}^0\varphi_x(x \pm x_0)$ (${}^0\Phi_v$ divided by the vibrational Wf, ${}^0\varphi_x(x \pm x_0)$ for the mode x, to be described below) in Eq. 13, their additive combinations are taken to be totally symmetric, leaving the factor, $\pm$, to the remaining part with the variables, x and ρ only. Therefore, the sign of $\pm$ is applied only to the parts, ${}^0\varphi_x(x \pm x_0)^t\Phi_t(\rho)$ to give rise to a new expression,

$$\begin{aligned} {}^{0/1,0,t}\Psi_\pm = {}&{}^{0/1}\psi_e(\{q\};\ \{Q_v\}',\ x,\ \rho)^0\Phi_v{}'(\{Q_v\}';\ x,\ \rho) \\ &\times 2^{-1/2}\{{}^0\varphi_x(x - x_0)^t\Phi_t(\rho) \\ &\pm {}^0\varphi_x(x + x_0)^t\Phi_t(\rho + \pi)\}, \end{aligned} \quad (15a)$$

with an achievable definition of

$${}^0\Phi_v{}' = {}^0\Phi_v/{}^0\varphi_x(x \pm x_0) \quad (|x| = \mp x), \quad (15b)$$

regardless of the value (sign) of x. This may be the simplest possible basis set to be used for interpreting the spectral data. (This may also be compared to the Wf's of HMA, as derived by Sanders, with a model hamiltonian as a two-dimensional

problem.[22]) We may also assume that ${}^0\Phi_v'$ is not dependent on x within the harmonic approximation, though not always being applied to the four kinds of peculiar modes, including the other two vibrational modes of the proton, as contained in ${}^0\Phi_v'$. Thus, the last braced factor in Eq. 15a with the $\pm$ sign in it, representing the pseudo torsional motion on the potential surface with C_6 symmetry (torsion accompanied by tunneling/warp), must belong to any species in G_{12} MSG. They can be identified by examining/drawing their functional shapes, e.g. as a combination of the full version of Fig. 4 of Ref. 15 (for MTrn$\cdot$H$_2$O) with Fig. 1 of Ref. 22 (for HMA in S_0), Fig. 10 of Ref. 15 (for MTrn in S_0), or else as a schematic expression of the potential surface (at least three-dimensional entity has to be imagined), while consulting the character table of G_{12}. This is one of the aims of Table 1, as presented before, where the data of the $+$ states are found in the column of $\Gamma(G_{12})$. It has to be noted that the contents in this column were originally obtained for the general G_{12} system without an intramolecular hydrogen bond, i.e. with its parent group belonging to C_{2v} MPG. As for the $-$ states, their species are confirmed to be equal to those acquired by multiplying each species in it with a_1'', whose products are given in the column of $\Gamma(G_{12}) \times a_1''$. However, even after this procedure, the degeneracy of the $K_i = 2$ level (originally of ${}^t\Phi_t$) is still retained as e' (though revealed in the parentheses in this Table 1). Therefore, we have to take the V_C term in Eq. 12 into account to reduce its degeneracy. The first trial may used be to solve a set of Schrödinger Eqs. for the coupled pair of Wfs $\{{}^0\varphi_x, {}^t\Phi_t\}$ with the hamiltonian including two kinds of terms $\{{}^{0/1,0}E(x,\rho), V_C\}$, where ${}^{0/1,0}E(x,\rho)$ is the eigenvalue corresponding to ${}^{0/1}\psi_e\,{}^0\Phi_v'$. However, the degeneracy of ${}^t\Phi_t$ cannot be removed as long as we attempt to retain the form of the Eq. 15a.

In this way, we are now forced to appeal to the TVC term of Eq. 4c to be found in V_C, so that the observed splitting of the $2E$ levels into pairs of $2E_a$ and $2E_b$ levels can be interpreted. This has to be based on the assumption that any one of the e' vibrational modes in the methyl group (top) is not strongly coupled with those in the frame of a rigid plane being composed of a seven-member (aromatic) ring with a conjugated electronic structure, while its vibrational frequency is modulated with both kinds of large-amplitude modes, so that its degeneracy is practically retained. (This is in accord with the general discussion in subsection 1.3.3, and is in contrast to the cases of NMn and HMA. Unfortunately, the experimental data of the high-frequency modes of MTrn are not available to endorse this assumption.) In actuality, this TVC term applies only partially to Eq. 15, i.e. to its portion of

$$ {}^{0,t}\Phi_{\pm}{}^{r} \equiv 2^{-1/20}\varphi_r\{{}^0\varphi_x(x-x_0){}^t\Phi_t(\rho) \pm {}^0\varphi_x(x+x_0){}^t\Phi_t(\rho+\pi)\}, \quad (16) $$

with its resultant splitting, i.e. its change (not of ${}^0\varphi_r$) from that for the e'/e'' state to that for the pair of the a_1'/a_1'' and a_2'/a_2'' states, corresponding to the sign ($\pm$) of the combination. In this way, all levels that were labeled with such as $0A^+$, $1E^-$, $2E_a{}^-$, and so on with superscripts ($+/-$) and subscripts (a/b) in Ref. 15 can now be assigned with the symmetry species in G_{12} MSG with the optional sign ($\pm$) of the combination, which may/need not coincide with those as indicated in Fig. 5 of Ref. 15. Here, attention has to be paid in practicing this procedure: (1) The species of the $+$ and $-$ states are given in the column of $\Gamma(G_{12})$ and $\Gamma(G_{12}) \times a_1''$, respectively, as already mentioned. (2) The assignments of the bands in their Fig. 5 should be done based on the principle of the common symmetry species in each hole-burning spectrum (as a sorted-out progression in the allowed $S_1 \leftarrow S_0$ transition), not withstanding the sign of $\pm$. Though not identified by them, a similar splitting of the $2E$ levels (in the S_0 state) could be perceived in the dispersed fluorescence spectra, if the observation was made at higher resolution, e.g. with a jet of lower vibrational (torsional) temperature, since the above procedure is commonly applicable to both the S_0 and S_1 states (the ab initio calculation being reported only for the S_0 state).

In concluding this section, a comment on their temporary interpretation of the splitting as being due to coupling between the torsional and proton-tunneling modes[15] should be made. Within the present formalism, it cannot literally lift the degeneracy with the selectivity of $K_i = 2$, as described above, merely giving rise to a splitting into a pair of e' and e'' symmetries because $e' \times a_1'' = e''$. Therefore, any other formalism quite different from that presented in this section might have been called for, whose search by the present author was a failure. One of the other approaches may be based on the assumption of tunneling among the 6 minima (not always consistent with the potential curve of Fig. 4 in Ref. 15), as had actually been applied for the lower 4 and 8 "torsional" levels of HMA[22] and NMP,[20,21] respectively. However, these systems are quite different from MTrn and from each other, e.g. with significant differences in the shapes/heights of the potential sufaces/barriers. (Good correspondence between MTrn and MTrn$\cdot$H$_2$O is the peculiarity in the present systems. In this respect, an extended description will be made of NMP in the next Section.) It should also be mentioned that the anomalous splitting of the $2E^{\pm}$ levels has never been interpreted by others, even in the most recent paper involving a theoretical calculation.[23] Thus, the present TVC scheme remains as the only one possible, unless the coupling between the torsion and the rotation with an exchange of their angular momenta is extraordinarily large to cause the apparent splitting of the former. No such report appears to have been made for the lower torsional levels in any other system.

3. Further Remarks

The interpretation of the experimental results for the title systems has been completed, in the above Section. However, remarks should be made on related systems so as to endorse the above conclusions, in a form to emphasize that one of the purposes of this paper is to provide a novel and useful device (such as know-how for finding an adequate basis set for each system) for spectroscopist to investigate methyl-substituted molecules, like those defined in the title.

(1) Most remarkable is the difference of the present G_{12} system from the G_6 system, such as MTrn$\cdot$H$_2$O. This is because a similar TVC term should exist for the G_6 system too, just as in the above G_{12} system, i.e. similar to Eqs. 4a and b:

$$^{6}V_{vt}{}^{r} \propto S_{ra}\cos\rho - S_{rb}\sin\rho, \quad (17a)$$
$$\propto S_r{}^{+}\exp(i\rho) + S_r{}^{-}\exp(-i\rho), \quad (17b)$$
$$\propto \Delta r\exp(i(\alpha+\rho)) + \Delta r\exp(-i(\alpha+\rho)) \quad (\propto \Delta r\cos(\alpha+\rho)). \quad (17c)$$

This can be derived by consulting the relationship $e \times e = a_1 + a_2 + e$. In this formulae, with a replacement of 2ρ by ρ in Eq. 4c, coupling matrix elements to remove the degeneracy of the e-type vibrational levels/modes emerge with $\Delta k_i = \pm 1$ instead of ± 2. Thus, TVC in this case is expected to be much (more than several times) stronger than the G_{12} system. Actually, the IR spectrum of ethanal (acetaldehyde, another G_6 molecule) vapor indicates evidence of a splitting of the three kinds of e modes/levels, similar to the case of NMn, with a clear resemblance to the IR spectrum of liquid ethanal,[24] which should be described with C_s MPG, rather than G_6 MSG. The C_3 symmetry of (the potential curve about) its torsional mode is no longer maintained in the condensed phase due to intermolecular interactions reducing the rate of the tunneling through the barrier (i.e. simultaneous warp of the three protons). Incidentally, the established force-field analysis for (free) ethanal is performed based on C_s MPG[25] against G_6 MSG. Accordingly, no more coupling scheme to split the e levels of the torsional mode is found. Namely, Eq. 17 no longer works to cause a splitting of the torsional levels, the e-type vibrational modes in the methyl group not being available. This is consistent with the observation in MTrn·H_2O, as described above.[15]

(2) Another system to be mentioned is the 7-azaindole dimer (7-AzI_2), identified as a C_{2h}(M) system, due to such as the involvement of proton tunneling modes of large amplitudes.[26] Its electronic spectra were interpreted by assuming the Frenkel-type exciton state in the weak-coupling limit, as expressed by

$$\Psi^{*v\pm}_{ABP} = 2^{-1/2}(\psi_{A^*}\Phi^0_{A^*}\psi_B\Phi^0_B\Phi^{v_P}_{A^*BP} \pm \psi_A\Phi^0_A\psi_{B^*}\Phi^0_{B^*}\Phi^{v_P}_{AB^*P}). \quad (18)$$

This Wf is derived in correspondence to a partitioned form of the exact hamiltonian into those of two constituent 7-AzI^- ions (A, B) and a part of two protons (P) and the other perturbation terms, with symbolically represented variables:

$$H_{ABP} = H_A(q_A,\ Q_A;\ \rho) + H_B(q_B,\ Q_B;\ \rho) + H_P + T_\rho + V_{AP} + V_{BP} + V_{AB};$$
$$H_P = T_P + V_P, \quad V_P = e^2/(4\pi\varepsilon_0 R_P). \quad (19)$$

It has to be noted that this set of Wf's of Eq. 18 has a formal resemblance to the present Eq. 13 and others, as was derived for MTrn. Actually, the procedure for deriving the present Eqs. 15a and b is just in parallel with section 2.2 of Ref. 26. Thus, MSG is proved to be a prerequisite in describing this kind of system, i.e. with large-amplitude modes to destroy the BO-type approximation.

(3) The next system to be mentioned is NMP, which also belongs to G_{12} MSG, and had been supposed to have a forbidden $S_1(A_2') \leftarrow S_0(A_1')$ (3s $\leftarrow \pi$ Rydberg or $\pi\sigma^*$) transition, where several inducing modes of various symmetry species as well as the involvement of the torsional mode are observed.[4,20,27,28] Very recently, however, the author found that the S_1 state should be ascribed rather to the $\pi\pi^*$ state (admixed with the $\pi\sigma^*$ states of 3s and 3p types of the common symmetry species of A_2'), at least for the potential minimum, as based on an ab initio calculation.[20,21] It was confirmed to be trapped in deep potential minima at a nonplanar and staggered conformation with the A'' symmetry of a C_s MPG. Thus, lower "vibrational" levels in the S_1 state were shown to be tunnel-split levels with various symmetry species for the G_{12} MSG. with the general formula

$$^{e(=1),v}\Psi = {}^1\psi_e(\{q\};\ \{Q_v\})^v\Phi_v(\{Q_v;\ X\}), \quad (20)$$

$^v\Phi_v(\{Q_v;\ X\})$ indicating any left term in Eqs. (A4)–(A7) in the Appendix of Ref. 20. These were constructed by consulting the character table of G_{12}, where X stands for any symmetry species of the G_{12} MSG. This may be taken as one of the results of generalization of what was presented in the above section 2.3. Based on this finding, the spectral data, as reported by Philis,[27] were reassigned while applying the formalism in the Appendix. As already announced in some detail,[4] the scheme of VC (VEC and TEC) in NMP involving both types of coupling modes will be discussed in the future.[21] Namely, this will be performed while extending the formalism, i.e. while applying the morphing technique for the ρ-dependency, and then allowing for a variation of $\{Q_v\}$ with the AO-following-nuclei scheme, in conformity to the BO-type approximations concerning to the three kinds of terms (of VEC, TEC, and TVC), as based on the ab initio calculation. With this morphing technique, the interaction/mixing of the vibrational modes between the top and the frame could be taken into account, even at the zeroth order.

(4) The last system is p-toluidine (p-methylaniline, pMA), which may possess 3 kinds of large-amplitude modes, i.e. the torsion of the methyl group, and the inversion and torsion of the amino group. Therefore, it could have a symmetry belonging to G_{24} MSG, as judged by Yan and Spangler.[29] However, with no evidence of tunnel splitting due to the torsional mode of the amino group[29–32] (probably because of its extremely high potential barrier), it should rather be described with G_{12} MSG belonging to the main title of this paper, as assumed by Tan and Pratt.[31] According to ab initio calculations,[32–34] the zero-point energy level in the S_0 state is supposed to be distributed over two kinds of minima of staggered and eclipsed (concerning to the two substitutes)[32] conformations, i.e. over $2 \times 6 = 12$ minima. They both have a C_s symmetry of MPG, whose symmetry plane is vertical to the molecular plane, where two hydrogen atoms attached on the N atom are displaced out of the molecular plane. While in the S_1 state,[32,33] the amino group is flattened to form a perpendicular conformation[32] with C_s symmetry, just corresponding to the C_s-staggered conformation of NMP in the ground state. By taking account of these kinds of structural information, the Wf's of the lower vibrational levels in the ground state of pMA could be most adequately described with

$$\Psi_\pm(q,\ \{Q_v\},\ \phi,\ \alpha) = 2^{-1/2}\{\psi_e{}^u(q;\ \{Q_v\},\ \phi,\alpha)\Phi_v{}^u(\{Q_v\};\ \phi,\ \alpha)\Phi_i{}^u(\phi;\ \alpha) \pm \psi_e{}^d(q;\{Q_v\},\ \phi,\ \alpha)\Phi_v{}^d(\{Q_v\};\ \phi,\ \alpha)\Phi_i{}^d(\phi;\ \alpha)\}^t\Phi_t(\alpha), \quad (21)$$

based on which the interpretation of the spectral data of such as Fig. 8 in Ref. 29 should be made.[35] Here, the notations of Wf's are practically the same as those given previously in Eqs. 2, 13, 15, 16, 18, and 20, with (u, d) representing the directions (up and down) of the displacement for the NH_2 group, while i (ϕ) and t (α) represent the inversion and torsion (angles) in the NH_2 and CH_3 groups, respectively. The similarities and differences should be noted among these Eqs., i.e. the zeroth-order expressions of the Wf's, as the evidence of what was stated at the end of the first paragraph in the Introduction.

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