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A Hybrid Program for Fitting Rotationally Resolved Spectra of Floppy Molecules with One Large-Amplitude Rotatory Motion and One Large-Amplitude Oscillatory Motion

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Abstract

A new hybrid-model fitting program for methylamine-like molecules has been developed, based on an effective Hamiltonian in which the ammonia-like inversion motion is treated using a tunneling formalism, while the internal-rotation motion is treated using an explicit kinetic energy operator and potential energy function. The Hamiltonian in the computer program is set up as a 2×2 partitioned matrix, where each diagonal block contains a traditional torsion-rotation Hamiltonian (as in the earlier program BELGI), and the two off-diagonal blocks contain tunneling terms. This hybrid formulation permits the use of the permutation-inversion group G_6 (isomorphic to C_{3v}) for terms in the two diagonal blocks, but requires G_{12} for terms in the off-diagonal blocks. The first application of the new program is to 2-methylmalonaldehyde. Microwave data for this molecule were previously fit using an all-tunneling Hamiltonian formalism to treat both large-amplitude-motions. For 2-methylmalonaldehyde, the hybrid program achieves the same quality of fit as was obtained with the all-tunneling program, but fits with the hybrid program eliminate a large discrepancy between internal rotation barriers in the OH and OD isotopologs of 2-methylmalonaldehyde that arose in fits with the all-tunneling program. This large isotopic shift in internal rotation barrier is thus almost certainly an artifact of the all-tunneling model. Other molecules for application of the hybrid program are mentioned.

Keywords

2-methylmalonaldehyde; Group theory; Hybrid fitting Hamiltonian; Hydrogen-transfer; Internal rotation; Tunneling formalism

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Supporting information: Table S1, showing computer output for expectation values of the symmetry operations a^3 and b ; Table S2, showing computer output of the final least-squares fit for 2-MMA-d0; Table S3, showing computer output of the final least-squares fit for 2-MMA-d1.

1. Introduction

Effective tunneling-rotational Hamiltonians, where all low-order terms allowed by group theory are considered for inclusion in the Hamiltonian operator, have been relatively successful in fitting microwave and other spectral measurements nearly to experimental error for a wide variety of molecules with two or more large-amplitude motions (LAMs), e.g., hydrazine,¹ methylamine,² water dimer,³ methanol dimer,⁴ dimethyl methylphosphonate,⁵⁻⁶ and the S_1 electronic state of acetaldehyde.⁷ Such tunneling treatments, however, have a number of well-known weak points: (i) Tunneling Hamiltonians cannot treat levels near or above the top of the barrier to the tunneling motion. (ii) Tunneling-rotational levels belonging to different large-amplitude and/or small amplitude vibrational states must be treated separately, since it is nearly impossible to accurately relate tunneling parameters for one vibrational state to those for another vibrational state. (iii) The physical meanings of the various coefficients in the phenomenological tunneling Hamiltonian are often obscure, especially for coefficients of higher-order terms.

In Sections 2-5 of this paper we present a new hybrid effective-Hamiltonian formalism for one of the molecular examples mentioned above, namely methylamine-like molecules. In this hybrid formalism the back-and-forth (oscillatory) umbrella motion, or its analog in other molecules, is still treated by a tunneling formalism, while the internal rotation motion is treated using a formalism containing explicit expressions for the kinetic energy operator and the three-well potential energy operator. Such a formalism allows us to calculate all torsional states having the same umbrella-motion quantum number simultaneously, in much the same way that all torsional states are calculated simultaneously in the simpler problem of a methyl-top internal rotation in a molecule with no other large-amplitude motions.

As reviewed in more detail in Section 6, an unresolved problem that remained⁸⁻⁹ in the comparison of internal-rotation tunneling splitting parameters for the OH and OD isotopologs of 2-methylmalonaldehyde (which differed by much more than expected) disappears when the present program is used in Section 7 to treat the same set of experimental measurements as in Ref.⁹. A brief discussion of the performance of this hybrid program and of other potential applications is given in Section 8.

2. Comparison of the ideas underlying a pure tunneling Hamiltonian with the ideas underlying a hybrid Hamiltonian

2.1. The pure-tunneling Hamiltonian formalism

The basic steps in setting up a tunneling Hamiltonian are: (i) to find all the different, but symmetrically equivalent equilibrium frameworks (i.e., minimum-energy conformations) that exist when the atoms are numbered, and to attach to each of these frameworks its own set of vibrational and rotational wavefunctions and energy levels, (ii) to find all the feasible tunneling paths that exist between various pairs of these frameworks, (iii) to use group theory to determine the set of non-symmetry-related paths (i.e., to determine the number of independent tunneling parameters), and (iv) to set up and diagonalize a Hamiltonian matrix based on this information.

Methylamine and 2-methylmalonaldehyde (2-MMA) are of interest from a large-amplitude-motion and tunneling point of view, because they both have a back-and-forth motion that triggers a 60° corrective internal rotation of the methyl group. The six energetically equivalent molecular frameworks that are sampled by the large-amplitude motions in this kind of molecule can be visualized for 2-MMA with the help of Fig. 1. Three of the six frameworks correspond to equilibrium values of the methyl-group internal-rotation angle α for the negative equilibrium value ($\gamma = -\gamma_0$) of the back-and-forth variable in the molecule, i.e., $\alpha = 0^\circ$, 120° , and 240° , as indicated on the left in Fig. 1. The other three frameworks correspond to equilibrium values of the internal-rotation angle α for the positive equilibrium value ($\gamma = +\gamma_0$) of the back-and-forth variable in the molecule, i.e., $\alpha = 60^\circ$, 180° , and 300° , as on the right in Fig. 1.

The quantum mechanical treatment used in pure tunneling formalisms is based on the idea that a complete set of vibration-rotation states localized in one minimum will interact with the equivalent complete set of vibration-rotation states localized in some neighboring minimum. The minima in the potential surface associated with the six frameworks of the previous paragraph are represented schematically in Fig. 2. These six minima are connected by two types of tunneling paths. Both types involve some internal rotation, but only one type involves the back-and-forth motion. Consider first the pure internal-rotation tunneling, where the methyl group angle α changes by 120° , while the back-and-forth coordinate γ remains unchanged. This tunneling is illustrated by the wide arrow below the molecular structures in Fig. 1, and by the horizontal red and blue arrows in Fig. 2. Consider next the back-and-forth (amino inversion or hydrogen transfer) tunneling motion, where the back-and-forth coordinate γ changes to its negative, while the methyl group angle α undergoes a “corrective internal rotation” of 60° to preserve its equilibrium orientation with respect to the amino group or hydroxyl hydrogen position in the molecule. This tunneling corresponds to going from (L) to (R) in Fig. 1, or vice versa. It is illustrated by the upward-pointing black arrows in Fig. 2.

The permutation-inversion (PI) molecular symmetry group is G_{12} . However, because of the introduction of an m -fold extended group $G_{12}^{(m)}$ to facilitate derivation of various phase factors for Hamiltonian matrix elements in the all-tunneling formalism,¹⁰ the tunneling paths connect $6m$ theoretically defined frameworks, as in Fig 2b of Ref.⁸.

It turns out that the concept of tunneling frameworks, as well as the complications of using an extended group both disappear in the hybrid formalism described in the next section, so that the hybrid formalism is conceptually simpler than the pure-tunneling formalism. One of the goals of this paper is to test this simpler formalism on a molecule whose energy levels are already “understood” from the pure-tunneling point of view.

2.2. The hybrid “tunneling plus non-tunneling” Hamiltonian formalism

The aim here is to arrive at an effective Hamiltonian which (unlike the pure-tunneling Hamiltonian above) is capable of carrying out a global fit to nearly experimental error of transitions involving the multitude of splitting components arising from several vibrational states of the methyl-top torsion (possibly including some above the torsional barrier), but involving only one vibrational state (often the ground state) of the back-and-forth tunneling

motion. In this formalism, the back-and-forth motion will be restricted to the moderate to high-barrier tunneling case, while the internal rotation motion will be allowed to have a high, intermediate, or nearly zero barrier.

The basic idea is to couple a tunneling formalism for the large-amplitude back-and-forth motion with a standard internal-rotation formalism for the large-amplitude rotatory motion of the methyl top. The principal conceptual difficulty in the hybrid formalism is caused by the loss of the concept of basis functions localized in the potential well of a given equilibrium framework. Pictorially this corresponds to not being able to draw arrows along a tunneling path from one minimum (i.e., from one point) on the potential surface to another (as was done in Fig. 2). Since the concept of localized basis functions is not present in the traditional (i.e., non-tunneling) internal-rotation formalism, a given internal-rotation function in the $+\gamma$ part of Fig. 2 must be thought of as spread out over all three wells. In an attempt to recapture some kind of pictorial image, we indicate this spreading out of the internal-rotation wavefunction by the two shaded strips in Fig. 3, and indicate the tunneling by an arrow going from the top strip to the bottom strip. From the point of view of Fig. 3, the quantum mechanics of the hybrid formalism must deal with tunneling from a “delocalized wavefunction” in the upper part of Fig. 3 to a “delocalized wavefunction” in the lower part, rather than tunneling from a given well (potential minimum) in the upper part to a given well in the lower part.

3. Coordinate system for the hybrid Hamiltonian and group-theoretical coordinate transformations

The system of molecule-fixed coordinates for methylamine can be defined as in Eqs. (1) to (8) of Section 2 of Ref.¹⁰. For 2-MMA, a few (relatively obvious) modifications are necessary. For example, the right side of the $i = 4,5$ row of Eq. (5) must be changed to $S^{-1}(0,-\gamma,0) \mathbf{a}_{11}^0$, so that it describes the transfer motion of H_{11} in Fig. 1, instead of the NH_2 inversion. Also, Eq. (9) of Ref.¹⁰ is not fully implemented here, because the rho-axis-method (RAM)¹¹ used in most modern computational procedures for the internal rotation problem¹² does not carry out a backward rotation of the whole molecule. Thus

$T^1(\gamma) \mathbf{a}_i'(\alpha, \gamma)$ in Eq. (9) of [10] is used as $\mathbf{a}_i(\alpha, \gamma)$ in Eq. (1).

Note that the procedure above defines only one molecule-fixed system of coordinates, which is to be used for all possible positions of the atoms in the laboratory. It thus differs from the molecule-fixed coordinates defined in some tunneling formalisms,³ where a separate set of molecule-fixed coordinates is defined for each equilibrium framework, i.e., different molecule-fixed coordinates are used to write the basis functions localized in different wells in the tunneling problem.

The group theory for methylamine and 2-MMA is nearly identical⁸ because: (i) if the methyl group in either molecule is temporarily replaced by an atom (i.e., by some spherically symmetric object), then both molecules maintain C_s point-group symmetry throughout their large-amplitude back-and-forth motion, and (ii) both molecules belong to the same PI group G_{12} . The present hybrid formalism and its associated fitting program can be used for any molecule having these characteristics.

The character table of the PI group G_{12} used for methylamine is given in Table 1 of Ref.¹⁰. The G_{12} character table used here for 2-MMA is given in Table 1 of Ref.⁸, where the abbreviated permutation symbol (45) in that table represents (45)(78)(9,10) in the atom numbering convention of Fig. 1. It happens that the molecular symmetry plane at equilibrium contains the c principal rotational axis for methylamine, but contains the b principal axis for 2-MMA. This leads to a slight complication in going from one of these molecules to the other, since the C_{2c} equivalent rotation, as defined in Ref.¹³, is associated with (23)(45)* in the character table¹⁰ for methylamine, but with (23)* in the character table⁸ for 2-MMA.

To avoid confusion resulting from these subtle differences, Table 1 gives group-theoretical coordinate transformations for the two operations that we use to generate the G_{12} PI group for 2-MMA. These generating operations are defined here as $a \equiv (123)(45)(78)(9,10)$ and $b \equiv (23)^*$. As usual when small-amplitude vibrations are ignored, only the transformation properties of the rotational angles χ , θ , ϕ , of the internal rotation angle α , and of the coordinate γ for the back-and-forth LAM are of interest here.

4. G_3 , G_6 , and G_{12} group-theoretical symmetry species of Hamiltonian operators, basis functions, and final eigenfunctions

To simplify notation in the equations in this paper, we represent internal rotation by the letter (or superscript) t (for torsion), the back-and-forth LAM by w (originally for wagging of the $-NH_2$ group in methylamine), and overall molecular rotation by r . It turns out that three PI groups are useful when discussing the Hamiltonian. The smallest PI group G_3 is isomorphic with the point group C_3 , and contains only the elements $a^2 = (132)$, $a^4 = (123)$, and $a^6 = e$ obtained from even powers of the generator a in Table 1. This is the group used in the program to block-diagonalize the full Hamiltonian into an A-species matrix and an E-species matrix. Elements in these two matrices are calculated from the same molecular constants, but the matrices are diagonalized separately. The A matrix yields all the nondegenerate twr energy levels and wavefunctions; the E matrix yields all the doubly degenerate twr energy levels and wavefunctions.

The intermediate PI group G_6 is isomorphic with the point group C_{3v} , and contains the elements e , a^2 , a^4 and $b = (23)^*$, a^2b , a^4b obtained from Table 1. This is the PI group commonly used for internal rotation problems in one-top molecules with a plane of symmetry at equilibrium. We show below that it can be used here (carefully) for some symmetry considerations of torsion-rotation operators that do not involve tunneling from the $\gamma > 0$ to the $\gamma < 0$ part of the potential surface in Fig. 3. Such operators correspond to those found in a traditional one-top C_s internal-rotation Hamiltonian.

The complete feasible PI group G_{12} for methylamine or 2-MMA is isomorphic with the point groups C_{6v} and D_{3h} , as indicated in Table 1 of Ref.⁸. It contains all elements obtained from powers and products of the two generators in Table 1: e , a , a^2 , a^3 , a^4 , a^5 and b , ab , a^2b , a^3b , a^4b , a^5b . All torsion-wagging-rotational operators allowed in the Hamiltonian must be totally symmetric in this group.

4.1. Partitioned structure of the Hamiltonian matrix

The two-step diagonalization procedure used here is essentially the same as that used in the one-top BELGI program.^{12,14} The torsion-K-rotation Hamiltonian matrices used in the first diagonalization step are also similar to those in Refs.^{12,14}. The full torsion-wagging-rotation Hamiltonian matrices used in the second diagonalization step of our program for this problem of two LAMs and overall rotation has a structure that is superficially similar to the partitioned Hamiltonian matrix used earlier to discuss the 509 cm⁻¹ fundamental vibrational state of acetaldehyde embedded in a bath of torsional states built upon the ground vibrational state.¹⁵ We first separate the set of non-degenerate states (of species ${}^{twr}A_1 \oplus {}^{twr}A_2 \oplus {}^{twr}B_1 \oplus {}^{twr}B_2$) from the set of doubly degenerate states (of species ${}^{twr}E_1 \oplus {}^{twr}E_2$) using the $\sigma = 0$ and $\sigma = +1$ characters associated with irreducible representations of the group C₃, and then write a separate Hamiltonian matrix for these two sets in the symbolic form

$$\begin{bmatrix} H_{RR} & H_{RL} \\ H_{LR} & H_{LL} \end{bmatrix}, \quad (1)$$

where each of the four sub-matrices in Eq. (1) is square, and all four have the same row and column dimension.

H_{RR} is the torsion-rotational Hamiltonian for 2-MMA when the hydroxyl hydrogen is localized in a well on the positive side of the γ axis. This Hamiltonian is the same as that used in the program BELGI-Cs,¹⁴ and has a row and column dimension equal to $(nvt) \times (2J + 1)$, where nvt is the number of torsional eigenfunctions kept after the first diagonalization,^{12,14} and J is the total angular momentum quantum number of the manifold being considered at any one moment. H_{LL} is the torsion-rotational Hamiltonian when the hydroxyl hydrogen is localized in a well on the negative γ axis. Group-theoretical arguments below show that matrix elements in this Hamiltonian have the same magnitude as elements in the corresponding positions in H_{RR} , but that some of the signs must be changed. For this reason the structure of the partitioned H matrix here is different from that in Ref.¹⁵.

H_{RL} and H_{LR} contain matrix elements (with their associated torsional and rotational dependences) that describe the hydroxyl hydrogen tunneling from the positive region of γ to the negative region, or vice versa, i.e., describe the $-O-H \cdots O= \rightarrow =O \cdots H-O-$ motion. Since H must be Hermitian, $H_{LR} = (H_{RL})^{tr*}$.

4.2 General group-theoretical considerations

The two generating operations in Table 1 together with products of all of their powers generate the 12 symmetry operations of the PI group G₁₂ appropriate for this problem. Matrix elements occurring in all blocks of the Hamiltonian in Eq. (1) must therefore arise from terms in the Hamiltonian operator that are totally symmetric (A_1) in G₁₂.

Within the H_{RR} and H_{LL} blocks of the Hamiltonian in Eq. (1), however, the coordinate γ is fixed at either $+\gamma_0$ or $-\gamma_0$, respectively. This allows us to make a connection with the group theory used for the one-top problem,¹¹ since the group G₆ used for the one-top problem (generated by a^2 and b here) contains only operators that leave γ unchanged. The character

table for this $G_6 = C_{3v}$ group is well known and is given, for example, in Table 7 of Ref.¹¹. If we now consider only torsion-rotation operators (with no dependence on the wagging coordinate γ), we conclude that any such Hermitian operator of species A_1 in the group G_6 and invariant to time reversal (i.e., any operator used in the one-top C_s problem¹⁴) will give rise to matrix elements in the RR and LL blocks. There is a slight complication, however, because operators of species A_1 in G_6 can be of species A_1 or B_1 in G_{12} . Operators of species A_1 in G_{12} need no further discussion, but operators of species B_1 in G_{12} (such as $\cos 3\alpha$) are not allowed in the Hamiltonian. Such operators can be made A_1 in G_{12} by multiplying them by the wagging coordinate γ (which is also B_1 in G_{12}). Since expectation values for γ obey $\langle L|\gamma|L \rangle = -\langle R|\gamma|R \rangle$, the presence of this symmetry-required γ factor has the effect of changing the sign of some of the “BELGI” matrix elements when going from the RR to the LL block.

It may at first seem surprising that the three-fold internal rotation potential term $\cos 3\alpha$ cannot occur by itself in the Hamiltonian for the present problem, although this fact was already recognized 45 years ago by Tamagake et al. when studying the potential surface of methylamine.¹⁶⁻¹⁷ In the present formalism, all operators of the form $\gamma(^{tr}A)$ contain a torsion-rotation operator ^{tr}A of species B_1 in G_{12} . Since this species correlates with A_1 in G_6 , such operators will in fact all give rise to nonvanishing matrix elements within the RR and LL blocks of the Hamiltonian in Eq. (1). It may also seem surprising that the matrix element associated with $\cos 3\alpha$ changes sign between the RR and LL blocks. This sign change arises physically because minimum values of the potential function $(1 - \cos 3\alpha)$ are shifted by $\alpha = 2\pi/6$ from the minimum values of $(1 + \cos 3\alpha)$, as shown mathematically by $\cos 3(\alpha + 2\pi/6) = -\cos 3\alpha$, and as illustrated by the $+\gamma$ and $-\gamma$ rows of minima in the schematic potential surface given in Fig. 2.

Table 2 gives the symmetry species in G_{12} and G_6 of a number of basic operators, products of which can be used to make Hamiltonian operators which are Hermitian, invariant to time reversal (equivalent here to containing an even number of momentum operators), and of species A_1 in G_{12} . The torsion-vibration operators are assigned a “perturbation order” nlm following the rule that total order $= n = l + m =$ torsional order + rotational order.¹⁸ For the wagging operators γ and P_γ , which do not occur in Ref.¹⁸, we (somewhat arbitrarily) choose the order 0 because splittings associated with the hydrogen transfer motion in 2-MMA-d0 are much larger than splittings associated with the torsional motion.

Table 3 gives the symmetry species of two different types of torsional-wagging basis functions. Table 4 gives the symmetry species for two different types of rotational basis functions. All these symmetry species can be derived rather easily by applying the coordinate transformations in Table 1 to the various basis functions. In the program, these symmetry-adapted basis functions are not explicitly used. It is, however, possible to generate a printout of coefficients of basis functions of the type $\psi(\gamma - \gamma_0) \times \exp[(3k + \sigma)i\alpha] \times |J, K\rangle$ and $\psi(\gamma + \gamma_0) \times \exp[(3k + \sigma)i\alpha] \times |J, K\rangle$, by proper manipulation of eigenvector coefficients from the first and second diagonalization steps. The expressions in Tables 3 and 4 can then be used to determine from these coefficients the symmetry species of any given eigenfunction. For example, for a $^{tr}B_2$ function, the coefficients of the basis functions $\psi(\gamma - \gamma_0) \times \exp(3k_0 i\alpha) \times |J_e, K_e\rangle$, $\psi(\gamma - \gamma_0) \times \exp(-3k_0 i\alpha) \times |J_e, -K_e\rangle$, $\psi(\gamma + \gamma_0) \times \exp(3k_0 i\alpha) \times |J_e, K_e\rangle$, and $\psi(\gamma + \gamma_0)$

$\times \exp(-3k_o i\alpha) \times |J_e, -K_e\rangle$ (where the subscripts e and o indicate even or odd integer values for k , J , and K) must all be equal in magnitude, with the sign relations $+$, $-$, $+$, $-$, respectively. Similarly, for a $^{tw}E_2$ function, the coefficients of the two basis functions $\psi(\gamma - \gamma_o) \times \exp[(3k_o + 1)i\alpha] \times |J, k_e\rangle$ and $\psi(\gamma + \gamma_o) \times \exp[(3k_o + 1)i\alpha] \times |J, k_e\rangle$ must be equal, where k_e can take either the value $+K_e > 0$ or $-K_e < 0$. In the program we do not inspect these coefficients individually, but instead use them to calculate expectation values ($+1$ or -1) of the operator a^3 for all wavefunctions and of the operator b for nondegenerate levels only. These expectation values, which are in fact group theoretical characters for these operators, allow us to use Table 1 of Ref.⁸ to assign a G_{12} symmetry species to the numerical eigenvector for each energy level. Some examples of such expectation values are given in Table S1 provided as supporting information.

4.3 Application of symmetry considerations to Hamiltonian terms and matrix elements

It is convenient to divide terms in the Hamiltonian into three groups: (i) operators containing no odd powers of γ or P_γ , (ii) operators containing odd powers of γ , but no odd powers of P_γ , and (iii) operators containing odd powers of P_γ , but no odd powers of γ . Because the γ coordinate is treated using a tunneling formalism, this turns out in practice to be equivalent to considering: (i) operators with no dependence on either γ or P_γ , (ii) operators containing a factor γ , but independent of the conjugate momentum P_γ , and (iii) operators containing a factor P_γ , but independent of the coordinate γ . It is further convenient to choose phase factors such that the Gaussian-like ground-state vibrational basis function for the γ (oscillatory) degree of freedom localized near $+\gamma_o$ and the corresponding function localized near $-\gamma_o$ are normalized and are mirror images of each other about $\gamma = 0$. That is, we choose phase factors such that $^w\psi_R(\gamma) = \psi(\gamma - \gamma_o) \sim N \exp[-\beta(\gamma - \gamma_o)^2]$ and $^w\psi_L(\gamma) = \psi(\gamma + \gamma_o) \sim N \exp[-\beta(\gamma + \gamma_o)^2]$ obey

$$\begin{aligned} ^w\psi_L(\gamma) &= +^w\psi_R(-\gamma) \\ \langle ^w\psi_L(\gamma) | ^w\psi_L(\gamma) \rangle &= \langle ^w\psi_R(\gamma) | ^w\psi_R(\gamma) \rangle = 1 \\ \langle ^w\psi_L(\gamma) | ^w\psi_R(\gamma) \rangle &= \langle ^w\psi_R(\gamma) | ^w\psi_L(\gamma) \rangle > 0. \end{aligned} \quad (2)$$

Operators of the form $(\gamma P_\gamma + P_\gamma \gamma)^{(tr)A}$ need not be considered in either diagonalization step, because they can be shown to have zero matrix elements in all four blocks of Eq. (1).

4.3.1 Operators with no dependence on γ or P_γ —Consider first matrix elements of a torsion-rotation operator ^{tr}A with no dependence on γ or P_γ , which is also Hermitian, invariant to time reversal, and of species A_1 in G_{12} . Such tr operators (e.g., J_x^2 , $J_z P_\alpha$, or $\cos 6\alpha$ from Table 2) are also A_1 in G_6 and therefore occur in the torsion-rotation Hamiltonian for an ordinary one-top molecule with C_s symmetry at equilibrium. Their matrix elements can be represented schematically, for product basis functions of the form

$$^{trw}\psi = ^{tr}\psi ^w\psi, \quad (3)$$

using the R and L subscripts of Eq. (1), as

$$\left\langle ^{trw}\psi'_R \left| ^{tr}A \right| ^{trw}\psi''_R \right\rangle = \left\langle ^{tr}\psi'_R ^w\psi_R \left| ^{tr}A \right| ^{tr}\psi''_R ^w\psi_R \right\rangle = \left\langle ^{tr}\psi'_R \left| ^{tr}A \right| ^{tr}\psi''_R \right\rangle \quad (4a)$$

$$\langle trw\psi'_L | trA | trw\psi''_L \rangle = \langle tr\psi'_L | trA | tr\psi''_L \rangle \quad (4b)$$

$$\langle trw\psi'_R | trA | trw\psi''_L \rangle = \langle tr\psi'_R | trA | tr\psi''_L \rangle \langle {}^w\psi_R(\gamma) | {}^w\psi_L(\gamma) \rangle \quad (4c)$$

$$\langle trw\psi'_L | trA | trw\psi''_R \rangle = \langle tr\psi'_L | trA | tr\psi''_R \rangle \langle {}^w\psi_R(\gamma) | {}^w\psi_L(\gamma) \rangle. \quad (4d)$$

In the present formalism, matrix elements of a given Hamiltonian operator ${}^{tr}A$ in Eq. (4) are calculated explicitly and the coefficient of this operator is treated as a fitting parameter. The overlap integrals $\langle {}^w\psi_R(\gamma) | {}^w\psi_L(\gamma) \rangle$ in Eq. (4) are not explicitly evaluated; their (unknown) value is absorbed in the value of the empirically determined fitting parameter.

4.3.2 Operators depending on γ but not on P_γ —Consider next matrix elements of torsion-wagging-rotation operators of the form $\gamma({}^{tr}A)$, with no dependence on P_γ , which are again assumed to be Hermitian, invariant to time reversal, and of species A_1 in G_{12} . Matrix elements of such operators from Table 2 (e.g., $\gamma\cos 3\alpha$ or $\gamma(J_x J_z + J_z J_x)$) can be represented schematically in the product basis functions of Eq. (3) as

$$\langle trw\psi'_R | \gamma {}^{tr}A | trw\psi''_R \rangle = \langle tr\psi'_R | trA | tr\psi''_R \rangle \langle {}^w\psi_R | \gamma | {}^w\psi_R \rangle \quad (5a)$$

$$\langle trw\psi'_L | \gamma {}^{tr}A | trw\psi''_L \rangle = \langle tr\psi'_L | trA | tr\psi''_L \rangle \langle {}^w\psi_L | \gamma | {}^w\psi_L \rangle = -\langle tr\psi'_L | trA | tr\psi''_L \rangle \langle {}^w\psi_R | \gamma | {}^w\psi_R \rangle \quad (5b)$$

$$\langle trw\psi'_R | \gamma {}^{tr}A | trw\psi''_L \rangle = \langle tr\psi'_R | trA | tr\psi''_L \rangle \langle {}^w\psi_R | \gamma | {}^w\psi_L \rangle = 0 \quad (5c)$$

$$\langle trw\psi'_L | \gamma {}^{tr}A | trw\psi''_R \rangle = \langle tr\psi'_L | trA | tr\psi''_R \rangle \langle {}^w\psi_R | \gamma | {}^w\psi_L \rangle = 0. \quad (5d)$$

The zeroes in Eqs. (5c) and (5d) follow from the fact that the integrand ${}^w\psi_R(\gamma) \cdot \gamma \cdot {}^w\psi_L(\gamma)$ is an odd function of γ . Eqs. (5c) and (5d) thus show that operators of the type $\gamma({}^{tr}A)$ have no matrix elements in the H_{RL} and H_{LR} blocks of Eq. (1), i.e., such operators have no non-vanishing tunneling matrix elements. The minus sign in Eq. (5b) indicates that matrix elements of such operators are equal in magnitude, but opposite in sign in the RR and LL blocks of Eq. (1). (This sign change can be verified by making the variable change $\gamma \rightarrow -\gamma$ in the integral $\langle {}^w\psi_R | \gamma | {}^w\psi_R \rangle$ and then using the first equality in Eq. (2).) The integrals $\langle {}^w\psi_R | \gamma | {}^w\psi_R \rangle$ are not explicitly evaluated in the hybrid formalism; their values are absorbed in the fitting parameters.

4.3.3 Operators depending on P_γ but not on γ —Consider finally matrix elements of torsion-wagging-rotation operators of the form $P_\gamma({}^{tr}A)$, with no dependence on γ , which are again assumed to be Hermitian, invariant to time reversal, and of species A_1 in G_{12} .

(Invariance to time-reversal here requires that ^{tr}A contain an odd number of momentum operators.) Matrix elements of operators of this type from Table 2 (e.g., $P_\gamma J_y$ or $P_\gamma J_z \sin 3\alpha$) can be represented schematically in the product basis functions of Eq. (3) as

$$\langle {}^{trw}\psi'_R | P_\gamma {}^{tr}A | {}^{trw}\psi''_R \rangle = \langle {}^{tr}\psi'_R | {}^{tr}A | {}^{tr}\psi''_R \rangle \langle {}^w\psi_R | P_\gamma | {}^w\psi_R \rangle = 0 \quad (6a)$$

$$\langle {}^{trw}\psi'_L | P_\gamma {}^{tr}A | {}^{trw}\psi''_L \rangle = \langle {}^{tr}\psi'_L | {}^{tr}A | {}^{tr}\psi''_L \rangle \langle {}^w\psi_L | P_\gamma | {}^w\psi_L \rangle = 0 \quad (6b)$$

$$\langle {}^{trw}\psi'_R | P_\gamma {}^{tr}A | {}^{trw}\psi''_L \rangle = \langle {}^{tr}\psi'_R | {}^{tr}A | {}^{tr}\psi''_L \rangle \langle {}^w\psi_R | P_\gamma | {}^w\psi_L \rangle \neq 0 \quad (6c)$$

$$\begin{aligned} & \langle {}^{trw}\psi'_L | P_\gamma {}^{tr}A | {}^{trw}\psi''_R \rangle \\ &= \langle {}^{tr}\psi'_L | {}^{tr}A | {}^{tr}\psi''_R \rangle \langle {}^w\psi_L | P_\gamma | {}^w\psi_R \rangle \\ &= + \langle {}^{tr}\psi'_R | {}^{tr}A | {}^{tr}\psi''_L \rangle \langle {}^w\psi_R | P_\gamma | {}^w\psi_L \rangle \\ &= - \langle {}^{tr}\psi'_L | {}^{tr}A | {}^{tr}\psi''_R \rangle \langle {}^w\psi_R | P_\gamma | {}^w\psi_L \rangle \neq 0. \end{aligned} \quad (6d)$$

The zeroes in Eqs. (6a) and (6b) follow from the facts that: P_γ is Hermitian, P_γ goes into its negative under time reversal, and ${}^w\psi_R$ and ${}^w\psi_L$ are real. Eqs. (6a) and (6b) show that operators of the type $P_\gamma(^{tr}A)$ have no matrix elements within the H_{RR} and H_{LL} blocks of Eq. (1), i.e., such operators only have non-zero matrix elements that correspond to tunneling.

The plus and minus signs in Eq. (6d) follow from the fact that the Hermitian product $P_\gamma(^{tr}A)$ is invariant to time reversal, while the individual Hermitian operators P_γ and ^{tr}A are not. The (real) values of the integrals $i\langle {}^w\psi_R | P_\gamma | {}^w\psi_L \rangle$ are absorbed in the fitting parameters (where the initial factor of i comes from the fact that ^{tr}A in the product $P_\gamma(^{tr}A)$ must go into its negative under time reversal).

Note that because integrals of the type $\langle {}^w\psi_R(\gamma) | {}^w\psi_L(\gamma) \rangle$, $\langle {}^w\psi_R(\gamma) | \gamma | {}^w\psi_R(\gamma) \rangle$, and $\langle {}^w\psi_R(\gamma) | P_\gamma | {}^w\psi_L(\gamma) \rangle$ are never explicitly evaluated in the present tunneling formalism, it is not necessary to specify the exact form of the functions ${}^w\psi_R(\gamma)$ and ${}^w\psi_L(\gamma)$. It is, of course, necessary to know the symmetry properties of these matrix elements in the Hamiltonian matrix, and for that purpose it is sufficient to assume the formal transformation properties shown in Eq. (2). For the purpose of visualizing the behavior of these formally introduced basis functions in the γ coordinate, the authors found it helpful to think in terms of harmonic oscillator functions, e.g., $\omega_R(\gamma) = \psi(\gamma - \gamma_o) \sim N \exp[-\beta(\gamma - \gamma_o)^2]$. However, neither harmonic oscillator functions nor any more sophisticated vibrational basis functions representing ${}^w\psi_R(\gamma)$ are actually used in the program or in the algebraic formalism on which the program is based.

5. Comments on the program

5.1 Similarities to earlier programs in this series

Just as in the earlier Belgi-Cs program,¹⁴ the Hamiltonian matrix producing nondegenerate (A) eigenvalues is treated separately from the matrix producing doubly degenerate (E)

eigenvalues. This is accomplished by using torsional basis functions of the simple form $\exp[(3k+\sigma)i\alpha]/(2\pi)$. The integer k runs between the cutoff values $-k_{trunc}$ to k_{trunc} , where typically $k_{trunc} = 10$. The integer σ runs between the limits -1 to $+1$, where matrices are set up only for $\sigma = 0$ (A species in G_3) and $\sigma = +1$ (E_+ species in G_3), since eigenvalues for $\sigma = +1$ are degenerate with those for $\sigma = -1$ (E_- species in G_3).

Again, just as in Belgi-Cs,¹⁴ the Hamiltonian matrix is set up and diagonalized in a two-step procedure.¹² In the first step separate RR and LL blocks in Eq. (1) are set up and diagonalized for each σ and each K value in the range $-J$ to $+J$. In this step only $K = 0$ matrix elements can be considered, which in practice usually means that only the operator $F(P_\alpha - \rho J_z)^2 + (1/2)V_3(1 - \gamma \cos 3\alpha)$ is taken into account in the first-step diagonalization. Because the $R \leftrightarrow L$ motion is a tunneling problem, the molecular fitting parameters F , ρ , and V_3 (and any other parameters considered in this first-step diagonalization) have magnitudes in the RR block which are exactly the same as in the LL block (though the presence of the factor γ causes some of their matrix elements to have opposite signs in the two blocks). This first-step diagonalization essentially produces torsional functions labeled by a torsional “symmetry species” $\sigma = 0$ or 1 , a torsional quantum number v_t , a rotational projection quantum number K , and a “wagging quantum number” $v_w = R$ or L to indicate localization of the back-and-forth tunneling motion in one of the two available wells. These localized R and L functions can be represented by the linear combination of the torsional and wagging basis functions shown in Eqs. (7a) and (7b) below, respectively, with coefficients $A^{v_t K \sigma R}_k$ or $A^{v_t K \sigma L}_k$ that depend on v_t , K , σ , R or L, and k (with only k being summed over):

$$^w\psi_R(\gamma) = \sum_k A^{v_t K \sigma R}_k \exp[(3k+\sigma)i\alpha] \quad (7a)$$

$$^w\psi_L(\gamma) = \sum_k A^{v_t K \sigma L}_k \exp[(3k+\sigma)i\alpha] \quad (7b)$$

Again, just as in Belgi-Cs,¹⁴ the first-step eigenfunctions in Eq. (7) are multiplied by symmetric top rotational functions to generate the twr basis functions

$$^w\psi_R(\gamma) = \sum_k A^{v_t K \sigma R}_k \exp[(3k+\sigma)i\alpha] |JK\rangle \quad (8a)$$

$$^w\psi_L(\gamma) = \sum_k A^{v_t K \sigma L}_k \exp[(3k+\sigma)i\alpha] |JK\rangle, \quad (8b)$$

that are used to set up the full matrix in Eq. (1) for the second-step diagonalization. When setting up this second-step matrix, only the first nvt eigenfunctions in Eqs. (8a) and (8b) are retained, to reduce the dimension of the calculation from $2(2k_{trunc}+1)(2J+1)$ to $2(nvt)(2J+1)$. Since k_{trunc} is usually 10 and nvt is usually 7, this reduces the dimension by a factor of three.

The partitioned matrix for the second-step diagonalization in Eq. (1) is very similar to the partitioned matrix used in Ref.¹⁵ to treat two interacting sets of torsional levels, one built on the ground vibrational state, the other built on an excited small-amplitude vibrational state.

The differences from Ref.¹⁵ are: (i) H_{RR} and H_{LL} in Eq. (1) describe the internal rotation manifold in two equivalent wells in a tunneling problem, so that the molecular constants used in these two blocks must be exactly the same (although the matrix elements they generate may have sign differences). In particular, there is no vibrational offset of one block with respect to the other. (ii) H_{RL} and H_{LR} describe tunneling interactions between the two equivalent wells, so that only operators and matrix elements in the torsional and rotational degrees of freedom are specified and evaluated explicitly. Matrix elements in the tunneling (oscillatory) coordinate are not explicitly evaluated, but are implicitly included in the fitting parameters.

The use of this partitioned matrix formalism means that many of the storage arrays in the program will contain only the “R-part” or only the “L-part” of the basis functions or eigenfunctions, and that many of the do-loops in the program code will involve binary matrix products consisting of only one of these two parts on the left multiplied by only one on the right. Such thinking is implied, for example, in the a,b,c,d labels added to Eqs. (4a) - (6d), which indicate matrix elements occurring in the upper left, lower right, upper right, and lower left blocks, respectively, of the 2×2 partitioned Hamiltonian matrix.

5.2 Labeling of the eigenfunctions after diagonalization

Eigenfunction labeling after diagonalizing a complicated Hamiltonian in a large basis set is frequently a problem because of significant basis-set mixing, and the present program is no exception to this general rule. Fortunately, most of the basis-set mixing for calculations involving 2-MMA occurs because the molecule is a very asymmetric rotor ($\kappa \approx -0.04$). After some reflection, or alternatively after examining the eigenvalues and eigenfunctions, the following steps for an automatic, unique, and essentially conventional labeling procedure can be established.

(i) Determine the exact G_{12} symmetry species of each of the $2(2J+1)$ nondegenerate eigenfunctions by calculating the expectation value of the two operators a^3 and b . From Table 1 these group-theoretical operations have the following effects on the twr basis functions in Eq. (8).

$$a^3 \quad \psi_R(\gamma) \exp[(3k+\sigma)i\alpha] |J, K\rangle = (-1)^{(k+\sigma+K)} \psi_L(\gamma) \exp[(3k+\sigma)i\alpha] |J, K\rangle \quad (9a)$$

$$a^3 \quad \psi_L(\gamma) \exp[(3k+\sigma)i\alpha] |J, K\rangle = (-1)^{(k+\sigma+K)} \psi_R(\gamma) \exp[(3k+\sigma)i\alpha] |J, K\rangle \quad (9b)$$

$$b \quad \psi_R(\gamma) \exp[(3k+\sigma)i\alpha] |J, K\rangle = (-1)^{(J-K)} \psi_R(\gamma) \exp[-(3k+\sigma)i\alpha] |J, -K\rangle \quad (9c)$$

$$b \quad \psi_L(\gamma) \exp[(3k+\sigma)i\alpha] |J, K\rangle = (-1)^{(J-K)} \psi_L(\gamma) \exp[-(3k+\sigma)i\alpha] |J, -K\rangle. \quad (9d)$$

From Table I of Ref.⁸ we see that pairs of expectation values $\langle a^3 \rangle, \langle b \rangle = (+1, +1), (+1, -1), (-1, +1),$ and $(-1, -1)$ correspond to the G_{12} species $A_1, A_2, B_1,$ and $B_2,$ respectively. (ii) Determine approximate values for the $|K|$ quantum number of each nondegenerate

eigenfunction by finding the $|K|$ value of the largest squared coefficient in that eigenfunction (where the squared coefficients must be added together for $+|K|$ and $-|K|$ basis functions when $K = 0$). Because of extensive K mixing, these K values may not be correct, but because the main mixing in 2-MMA obeys $K = \pm 2$ selection rules, the even-integer versus odd-integer character of K will be correct. (iii) Divide these $2(2J+1)$ nondegenerate eigenfunctions into four groups, containing, respectively, even- K , A functions, odd- K , B functions, even- K , B functions, and odd- K , A functions. (iv) Order each group separately by energy, and assign K_a, K_c quantum numbers by energy ordering in the usual way.

This same procedure can be carried out for the degenerate E species eigenfunctions, except that here we consider only expectation values of $\langle a^3 \rangle = +1$ and -1 , which correspond to E_2 and E_1 species, respectively. Divide the $2(2J+1)$ E species eigenfunctions into four groups, containing even- K , E_1 functions, odd- K , E_2 functions, even- K , E_2 functions, and odd- K , E_1 functions. Order each group separately by energy and again assign K_a, K_c quantum numbers by energy ordering in the usual way.

We note in passing that the eigenvalue and eigenvector labeling problem will in general be more confusing for the present problem than it was for the two-vibrational-state problem treated in Ref.¹⁵, because the large vibrational energy difference of 509 cm^{-1} there corresponds to the much smaller (e.g., a few cm^{-1} or less) tunneling splitting of the oscillatory motion here. As a result, the rotational levels obtained in Ref.¹⁵ for J values commonly seen in room-temperature (or lower) spectra automatically fell into two well-separated energy groups, one clearly associated with H_{RR} in Eq. (1) (i.e., clearly associated with the R basis functions), the other clearly associated with H_{LL} . In contrast, rotational levels in the present problem consist of exactly 50-50 mixtures of the R and L basis functions. Furthermore, rotational levels from the two tunneling eigenstates here begin to be interleaved at very low J values.

5.3 The least squares fitting

A non-linear least squares fit is carried out, where derivatives of each eigenvalue E_i with respect to each molecular parameter P_j are calculated by the Hellmann-Feynmann theorem

$$\partial E_i / \partial P_j = \langle \psi_i | \partial H / \partial P_j | \psi_i \rangle. \quad (10)$$

It is convenient to use ab initio estimates for the structural parameters F , ρ , A , B , C and D_{ab} when starting a fit from the very beginning for some new molecule. Ab initio values for the torsional barrier V_3 and the back-and-forth splitting parameter (WAG2 in the program) may not be reliable enough to start a fit with no manual adjustment, however, so some trial and error may be necessary. For this purpose, we note from Eq. (5) of Ref.⁸ that transitions of the type shown in Fig. 2 of Ref.⁹ give energy differences that depend to first order only on the back-and-forth splitting and the rotational constants. Because transitions between degenerate and nondegenerate states are forbidden, there are no transitions that give direct information on the torsional splittings. Once the eight parameters above are approximately correct, fits in which relatively large sets of parameters are adjusted will often converge in less than 10 iterations.

The question frequently arises of which combination of parameters in the Hamiltonian should best be floated when trying to fit any given spectrum. For the present work, we relied only on intuition and trial-and-error to deal with this problem. The number of reasonable combinations can often be reduced in a systematic way, however, by using contact transformations to determine sets of “determinable parameters,” as was done for the torsion-rotation problem in molecules with one methyl top in Ref.¹⁸. We did not investigate this question here, but note only that this kind of treatment depends strongly on the assumed “order” for each of the operators in the Hamiltonian.¹⁸ As briefly noted in Table 2, we assigned order 0 to γ and P_γ . Another reasonable choice would be to assign order 1 to these two tunneling operators.

A second problem that frequently arises when fitting large data sets to a model with many parameters is whether the fit has converged to the global minimum or to some local minimum with a higher standard deviation or other undesirable properties.⁶ We converged to a number of local minima (also called false minima) during the fittings of 2-MMA using our new hybrid program. One example is briefly discussed in Section 8.1.

5.4 Checking of the program

Verifying that expectation values of a^3 and b in Eq. (9) calculated with the final eigenvectors have the values +1 or -1 to machine round-off error provides a check that the Hamiltonian terms used in the program have the correct symmetry properties. (See Supporting Table S1.)

All matrix elements occurring in the diagonal H_{RR} and H_{LL} blocks of Eq. (1) can be checked by comparing eigenvalues and eigenvectors obtained after diagonalization against those obtained from a calculation carried out with Belgi-Cs¹⁴ using the same molecular constants. Eigenvalues of H_{RR} and H_{LL} will agree exactly with those from Belgi-Cs, as will the eigenvector coefficients in H_{RR} . Eigenvector coefficients in H_{LL} will have some changes in sign, as implied by Section 4.3.

Checking the matrix elements in H_{RL} and H_{LR} presents more of a problem. If parameters are adjusted to correspond to the high-barrier tunneling limit, then the four $J = 0$ levels should lie at the appropriate place on the graph in Fig. 3 of Ref.⁹. Finally, however, a small program to calculate only $J = 6$ energy levels was written. In this program the Hamiltonian matrix was set up in the full basis set of $(2k_{trunc}+1)(2J+1)2 = 21 \times 13 \times 2 = 546$ functions, where matrix elements of all Hamiltonian terms can be easily checked by inspection. This matrix was then diagonalized in a single step, and its eigenvalues were compared with those obtained for $J = 6$ from the more elaborate two-step program described here with $nvt = 21$ (rather than 7).

Derivatives were checked as follows. If fits with a given set of floated parameters converged quickly, then derivatives of energies with respect to those parameters were assumed to be correct. When the convergence was unusually slow, or exhibited other suspicious behavior, then fits with only a single parameter floated were carried out to diagnose and fix the problem. It was helpful in some cases to compare derivatives calculated from Eq. (10)

against derivatives calculated numerically from $(E_1 - E_2)/(P_1 - P_2)$, where E_i is the energy calculated when parameter P has the value P_i (all parameters other than P being held fixed).

6. Three-fold barrier problem in previous fits of the OH and OD isotopologs of 2-MMA using the pure tunneling model

The spectral analyses of Ref.⁸⁻⁹ used a pure tunneling model to fit the observed microwave transitions of 2-MMA, so that the experimentally determined fitting parameters described tunneling splittings rather than barrier heights. When these fitting parameters were used to determine a purely torsional E – A energy difference, the counter-intuitive result emerged that the OH isotopolog had a torsional splitting of 334.5 MHz, while the slightly heavier OD isotopolog had a significantly larger torsional splitting of 1044.6 MHz. These splittings were almost the same in Refs.⁸⁻⁹, where two data sets of very different size and J , K distribution were fit to nearly experimental error using the same pure tunneling model, but using many more parameters for the more extensive and higher- J , higher- K data set. It was thus concluded that these tunneling-model splitting parameters were correctly determined from both a spectral assignment and a least-squares fitting point of view.

A few reasonable assumptions were then used in Ref.⁹ to convert these experimentally determined internal rotation splittings into V_3 barrier heights, with the result that $V_3(\text{OH}) = 401 \text{ cm}^{-1}$, while $V_3(\text{OD}) = 312 \text{ cm}^{-1}$. This large difference in barrier heights, after deuteration at a site rather far from the methyl group, could not be explained, leading to the suggestion that some problem might exist in the interpretation of the meaning of the experimentally determined fitting parameters in the multidimensional tunneling formalism.

Recently, some progress has been made in explaining this large discrepancy in V_3 by examining in more detail the concept of tunneling-parameter leakage,⁹ where values of large splitting parameters for certain tunneling motions leak into (or contaminate) values of much smaller splitting parameters for other tunneling motions. The theoretical expressions that seem to describe this leakage arise essentially from the non-zero overlap integrals that are an intrinsic property of tunneling-formalism basis functions. A number of poorly understood features remain in this theoretical treatment, however, so it is not yet ready for use in any attempt to give a full and convincing explanation for this phenomenon.

The hybrid-model fitting program of the present paper represents a parallel-track attempt to deal with this problem. In this approach the leakage of the large tunneling parameters associated with the hydrogen transfer motion into the small tunneling parameters associated with the internal rotation is prevented by simply removing all internal rotation tunneling parameters from the theoretical formalism and replacing them by a directly fitted barrier height V_3 . We shall see in the next section that $V_3(\text{OH}) \approx V_3(\text{OD})$ is indeed found when the present program is used.

7. Refitting of 2-MMA data sets from the literature

All 2-MMA data are taken from transitions given in the deposited supplementary material of Ref.⁹. We used those measured transitions and weights without change, so that meaningful

comparisons of the two different models could easily be made. Pickup problems (i.e., problems with assigning basis-set quantum numbers to highly mixed final eigenvectors) led to occasional differences in K_a values used in the present work and in Ref.⁹, as discussed in Section 8. Our final fits of the OH and OD isotopologs of 2-MMA are given in full in the supplementary material (Supporting tables S2 and S3). In this section we present mainly information needed for a discussion of these fits.

7.1 The 2-MMA-d0 fit

Table 5 gives the molecular parameters obtained from the present hybrid-model fit of the 2-MMA-d0 isotopolog, where we achieve the same quality of fit as in Ref.⁹, but with four fewer adjustable parameters. The distribution of parameters is similar to that in Ref.⁹, since the 20 nontunneling parameters in the upper part of Table 5 correspond to the 24 (= 14 non-tunneling + 10 torsional tunneling) parameters in Table 2 of Ref.⁹, while the 13 hydrogen-transfer tunneling parameters in the lower part of Table 5 correspond to the 13 hydrogen-transfer tunneling parameters in Ref.⁹. Some of the fitted parameters in the hybrid-model have essentially the same physical meaning as fitted parameters in the all-tunneling model, but they will nevertheless differ in value because of higher order contributions introduced by quantum mechanical differences in the two models. For example, corresponding values for the rotational constants A , B , C , and ρ in the two fits are within 1% of each other, while the parameter D_{ab} is larger than s_1 by about 34%.

The main difference between Table 5 and the results from Ref.⁹ is the fact that the internal rotation barrier height has dropped from $V_3(\text{OH}) = 400.7 \text{ cm}^{-1}$ in Eq. (3) of Ref.⁹ to $V_3(\text{OH}) = 302.4 \text{ cm}^{-1}$ in Table 5. This smaller barrier height is now reasonably consistent with the $V_3(\text{OD})$ value of 315.1 cm^{-1} determined here or the $V_3(\text{OD}) = 311.6 \text{ cm}^{-1}$ value determined in Ref.⁹. For this reason, we conclude that the hybrid-model formalism has fulfilled one of its original goals, in that it gives a consistent (and therefore presumably also reliable) estimate of V_3 for both isotopologs of 2-MMA.

This fact also lends support to the tunneling parameter leakage theory proposed in Ref.⁹. As explained there, the ratio of the hydrogen-transfer splitting parameter to the internal rotation splitting parameter is 188 for the d0 species, but only 8 for the d1 species, so that a small amount of leakage from the larger hydrogen-transfer splitting parameter into the smaller internal-rotation splitting parameter will cause a much greater numerical shift in the d0 species. This tunneling parameter leakage theory thus also predicts that the V_3 determined in Ref.⁹ for the d1 species should be much closer to the correct internal rotation barrier height, than is the V_3 determined for the d0 species. These conclusions are in agreement with the results obtained here using the hybrid-model Hamiltonian and fits.

7.2 The 2-MMA-d1 fit

Table 6 gives the molecular parameters obtained from the present hybrid-model fit of the 2-MMA-d1 isotopolog. Here we achieve a fit about 3% worse than in Ref.⁹, but with one less adjustable parameter. The distribution of parameters is again similar to that in the corresponding fit in Ref.⁹, since the 20 non-tunneling parameters in the upper part of Table 6 correspond to 21 (= 14 non-tunneling + 7 torsional tunneling) parameters in Table 3 of

Ref.⁹, while the 11 hydrogen-transfer tunneling parameters in the lower part of Table 6 correspond to the 11 hydrogen-transfer tunneling parameters in Ref.⁹. Fitted values for corresponding parameters in the two models are again at the level of agreement that can reasonably be expected.

In contrast to the result obtained for the OH isotopologs, the fitted value of $V_3(\text{OD}) = 315.36(14) \text{ cm}^{-1}$ obtained here is very close to the derived value of $V_3(\text{OD}) = 311.6 \text{ cm}^{-1}$ obtained in Eq. (3) of Ref.⁹.

7.3 Comparison with ab initio results

Gulaczyk and Kręglewski²⁰ recently carried out potential surface calculations for 2-MMA at the MP2/6-311++G** level and then calculated $J = 0$ energy levels on this surface using their semi-rigid model. In their Table 5 they compare the ab initio barrier height with values determined by refining their surface to fit (separately) experimental information for the d0 and d1 isotopologs from Ref.⁹. The internal rotation barriers they calculate in this way are 332.7 and 333.0 cm^{-1} , respectively. The nearly identical internal rotation barriers for the two different isotopologs obtained in Ref.²⁰, strongly support their treatment. The agreement with our values of 302.4 and 315.4 cm^{-1} is probably as good as can be expected at this time. In this connection, it should be noted that no experimental information on the torsional $\nu_t = 1 \leftarrow 0$ fundamental vibrational frequency is present in either model.

8. Discussion

8.1 Performance of the program

One way of assessing the performance of the present hybrid program is to look at the weighted standard deviation of its fit and at the number of fitted lines per fitting parameter. From this point of view, our d0 fit has a weighted standard deviation of $\sigma = 1.03$ and a ratio of 78 fitted lines per fitting parameter. Our d1 fit has of $\sigma = 1.11$ and 82 lines per parameter. A more careful evaluation of the fit quality (which we do not go into) would require examining the measurement uncertainty assigned to each measured transition, and determining the number of fitted energy levels (rather than lines) per fitting parameter.

Another way of assessing performance is illustrated in Table 7, which gives a comparison of our fits with the corresponding pure-tunneling-formalism fits in Ref.⁹. For the d0 isotopolog the present model gives the same standard deviation as Ref.⁹, but uses four fewer adjustable parameters. For the d1 isotopolog the present model gives a slightly worse standard deviation than Ref.⁹, but uses one less adjustable parameter. It turns out that we were unable to match the d1 standard deviation from Ref.⁹, even after many trial-and-error fits with several additional parameters.

A third way of assessing the performance of the program is to look at the number of pickup problems that occur. By “pickup problems” we mean the times that “wrong” basis-set quantum numbers are assigned to various heavily mixed final eigenfunctions that arise after diagonalization of a large Hamiltonian matrix containing numerous interactions among the basis functions. This was the case in the d0 isotopolog, for example, for approximately 26 of the eigenfunctions occurring as upper or lower states in the 2578 fitted transitions. Such

pickup problems had to be fixed manually, either by changing the upper or lower state K_a assignment of the observed transition in the input file, or by changing the K_a assignment given to the eigenvalue in the program. If one examines surrounding lines in the same branch, it often happens that one of these ways of changing K_a values appears to be better than the other. Since the present work involves refitting an existing spectrum, we did not examine each manual fix of a pickup problem to make sure that it was the “best” fix possible.

These pickup problems have a scientific origin, in the sense that rotational energy levels of an asymmetric rotor are known to organize themselves into near-prolate series at high K_a , with energies approximately given by $(1/2)(B+C)J(J+1) + [A - (B+C)/2]K_a^2$, and into near-oblate series at high K_c , with energies approximately given by $(1/2)(A+B)J(J+1) + [C - (A+B)/2]K_c^2$. For 2-MMA this already complicated asymmetric-rotor reorganization is further complicated by interactions and splittings associated with the two large-amplitude motions. It is for levels in the process of changing from the prolate to oblate limit that the pickup problems seem most severe. The asymmetric-rotor coupling cases described above can be pictorially understood by the common technique of plotting various reduced energy level expressions against $J(J+1)$. For the present case, these reduced energy levels take the form $E - B_{\text{eff}}J(J+1)$, with $B_{\text{eff}} = (B+C)/2$, $(A+B)/2$, and $(A+2B+C)/4$, when focusing on behavior in the near-prolate, near-oblate, and exactly-intermediate limits, respectively. Such plots of reduced energy levels ($E_{\text{reduced}} = E - B_{\text{eff}}J(J+1)$) against $J(J+1)$ for 2-MMA-d1 are shown in Supplementary Figs 1-3 with various values of B_{eff} to illustrate the various coupling cases.

A fourth way of assessing performance is to look at the tendency of the least-squares fit to fall into a local minimum and stay there. This is often a severe problem when fitting large data sets to many adjustable parameters, as we do with the present program. The probability of falling into a local minimum seems to be especially high when one starts the fit with a J,K distribution of data that is too large. In our d0 fits, for example, such a “shortcut” led to a weighted standard deviation of the fit of about $\sigma = 1.6$. It was only after getting a fit with $\sigma \approx 1$ for a data set with rather low J and K , and then slowly adding higher J and K transitions, while maintaining $\sigma \approx 1$ by simultaneously slowly adding additional constants, that the fit in Table 5 could be achieved.

8.2 Possible applications of the program to other molecules

As mentioned, the treatment of internal rotation in this hybrid program should make it possible to include all torsional levels built on a given “wagging” vibrational level in a single global fit. Since the microwave and infrared spectrum of methylamine (CH_3NH_2) has been extensively studied using the all-tunneling formalism,^{2,10,21-22} the literature contains extensive high-resolution information on the $\nu_t = 0$ and 1 CH_3 torsional levels in the NH_2 wagging ground state (i.e., the ground state of the back-and-forth motion). In addition, the ^{14}N -quadrupole splittings are relatively well understood, and “dehyperfine” rotational levels have been calculated. This molecule is thus a very favorable candidate for testing the many-torsional-level global fit capabilities of the program.

This program should also be able to fit microwave spectra of certain types of complexes. One class of complexes is illustrated by $\text{H}_3\text{N}\cdots\text{HOH}$,²³ where NH_3 is the internal rotor and

water proton exchange in the hydrogen bond is the back-and-forth motion. Spectral measurements for ammonia-water are rather extensive, but their measurement error (as estimated from several combination differences) is of the order of 1 MHz, and the model used in Ref.²³ is able to fit existing data to that accuracy. Lamb-dip measurements could presumably furnish more precise data, if static-cell conditions could be found where vapor-phase ammonium hydroxide is present in high enough concentrations. Published measurements on a closely related complex, namely $\text{CH}_3\text{CN}\cdots\text{HOH}$,²⁴ do not include any *b*-type THz transitions, and are therefore not extensive enough to test this model.

As a possible complication in these two water complexes, it should be noted that even though there are only two ways for an atom-labeled $\text{H}_1\text{-O-H}_2$ molecule to attach itself to the lone pair of the N atom in these two molecules, two distinct back-and-forth motions are in fact possible, both of which correspond to the (12) permutation operation. These consist either of a C_2 rotation about the H_2O principal inertial *b* axis, or of a (smaller) rotation about the H_2O principal inertial *c* axis. The present program is based on group-theoretical considerations that assume only one large-amplitude back-and-forth coordinate needs to be considered (e.g., the coordinate γ used throughout this paper). If in fact there are two independent back-and-forth large amplitude coordinates (γ_1 and γ_2 , say), then significant conceptual and algebraic changes in the present formalism will be required. On the other hand, if *ab initio* potential surfaces show that there is only one easily accessible tunneling path and saddle-point for the (12) hydrogen-bond exchange (i.e., only one large-amplitude tunneling coordinate, even if curvilinear), then the present program should be applicable to spectra of these complexes with little or no change.

A second class of complexes to which the program should be applicable are hydrogen-bonded acid pairs like acetic acid - formic acid ($\text{CH}_3\text{COOH} - - \text{HOOCH}$)²⁵ or the acetic acid - nitric acid ($\text{CH}_3\text{COOH} - - \text{HOONO}$) analog of $\text{HCOOH} - - \text{HOONO}$,²⁶ where the back-and-forth motion is the exchange of both protons in the double hydrogen bond of the complex. Here too, the relatively few existing measurements for the ground torsional state have been fit to experimental error (a few tens of kHz) using other models.

The general procedure of a hybrid Hamiltonian operator and a partitioned Hamiltonian matrix could in principle be extended to apply to molecules with more than one internal rotor and/or more than one back-and-forth motion. For example, a molecule with one rotor and two back-and-forth motions would require a 4×4 partitioned matrix, with essentially identical BELGI-type Hamiltonian matrices in each of the four diagonal blocks, and tunneling matrix elements connecting basis functions of the four frameworks in pairs in the off-diagonal blocks.

Supplementary Material

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Fig. 1.

(L) - An equilibrium framework of numbered atoms in 2-methylmalonaldehyde corresponding to an $O_7 - H_{11}$ hydroxyl group, and to a negative value of the hydrogen-transfer coordinate γ . (R) - An equilibrium framework of numbered atoms in 2-methylmalonaldehyde corresponding to an $O_8 - H_{11}$ hydroxyl group, and to a positive value of γ . Pure internal-rotation tunneling in either framework corresponds to rotating the methyl group at the bottom of the molecule by $\pm 120^\circ$, as suggested by the thick curved arrows. Hydrogen-transfer tunneling corresponds to breaking the $O_7 - H_{11}$ bond and forming the $O_8 - H_{11}$ bond, leading to a tautomeric rearrangement of single and double bonds, and to a corrective internal rotation of the methyl group at the bottom of the molecule by $\pm 60^\circ$. The atom numbering and axis labeling here is the same as in Fig. 1 of Ref.⁸. Frameworks with $\gamma < 0$ and $\gamma > 0$ are often referred to as (L) and (R) in the text. They are related by the permutation-inversion group operation $(123)(45)(78)(9,10)$.

Fig. 2.

A schematic representation of equal-energy contours surrounding the six minima on a two-dimensional potential surface for 2-methylmalonaldehyde. The internal-rotation angle α is plotted along the horizontal axis in degrees. The oscillatory (or back-and-forth) hydrogen-transfer coordinate γ is plotted along the vertical axis in arbitrary units. Pure internal-rotation tunneling between adjacent frameworks is represented by the two horizontal arrows. Hydrogen-transfer tunneling is represented by the two upward-pointing diagonal arrows. For more details on the use of a diagram like this to construct an all-tunneling Hamiltonian, see the text associated with Fig. 2 of Ref.⁸.

Fig. 3.

An attempt to indicate, by adding shading to Fig. 2, the loss of the concept of individual frameworks that occurs when internal-rotation basis functions of the form $e^{+i(3k+\sigma)\alpha}$ are used in the hybrid formalism. Such basis functions span the entire 2π range of α , so that the back-and-forth motion, i.e., the only tunneling motion remaining in the hybrid formalism, must be represented pictorially by a vertical arrow going from the $+\gamma$ upper strip in this figure to the $-\gamma$ lower strip. The purpose of the present paper is to turn Fig. 3 into a quantum-mechanical formalism.

Table 1

Group-theoretical transformations of the molecule-fixed coordinates used for 2-methylmalonaldehyde here and in the present fitting program

PI^a	Name ^b	CoM ^c	Rotation ^d	Torsion ^e	H-tr ^f	SAV ^g
E	<i>e</i>	R	$\chi, \theta, \varphi \rightarrow \text{E}$	α	γ	$d_i \quad i = 1, 2, 3, 4, 5, 7, 8, 9, 10$
(123)(45)(78)(9,10)	<i>a</i>	+R	$\chi + \pi, \theta, \varphi \rightarrow \text{C}_{2z}$	$\alpha - 2\pi/6$	$-\gamma$	$\text{C}_{2z} d_j \quad j(i) = 2, 3, 1, 5, 4, 8, 7, 10, 9$
(23)*	<i>b</i>	-R	$\pi - \chi, \pi - \theta, \pi + \varphi \rightarrow \text{C}_{2y}$	$-\alpha$	$+\gamma$	$\sigma_{xz} d_j \quad j(i) = 1, 3, 2, 4, 5, 7, 8, 9, 10$

^aPermutation-inversion generating operations for the G₁₂ group in Table 1 of Ref.⁸.

^bShorthand names *a* and *b* for the generating operations. When *a* and *b* act on the coordinates in row 1, they produce the transformed coordinates shown to their right. The operation *a* gives rise to the combined hydrogen-transfer and corrective internal rotation motion shown in Fig. 1.

^cLaboratory-fixed Cartesian coordinates of the center of mass in Eq. (1) of Ref.¹⁰.

^dRotational (Eulerian) angles in Eq. (1) of Ref.¹⁰. Equivalent rotations¹³ are given after the arrow.

^eThe LAM internal-rotation angle of the methyl top in Eqs. (1) and (5) of Ref.¹⁰.

^fThe LAM hydrogen-transfer coordinate in 2-methylmalonaldehyde, analogous to the amino inversion angle in Eqs. (1) and (5) in Ref.¹⁰.

^gDisplacement vectors d_i for the small-amplitude vibrations in Eq. (1) of Ref.¹⁰ must be replaced by a rotated or reflected vector d_j , where *j* is chosen as a function of *i* as indicated by the ordering in the *i* and *j*(*i*) rows. For both *a* and *b*, *j*(*i*) = *i* when *i* = 6, 11, 12. Displacement vectors are not considered further in this work.

Table 2

Symmetry species for various low-order operators

nlm^a	Op^b	G_{12}^c	G_6^d	nlm^a	Op^b	G_{12}^c	G_6^d
000	P_γ	B ₁	A ₁	110	P_α	A ₂	A ₂
000	γ	B ₁	A ₁	220	$\cos 3\alpha$	B ₁	A ₁
101	J_x	B ₂	A ₂	220	$\sin 3\alpha$	B ₂	A ₂
101	J_y	B ₁	A ₁	440	$\cos 6\alpha$	A ₁	A ₁
101	J_z	A ₂	A ₂	440	$\sin 6\alpha$	A ₂	A ₂

^aThe nlm ordering scheme of Ref. ¹⁸, where $n = l + m$, with l = order of the torsional factor and m = order of the rotational factor in the operator. We assign the wagging factors γ and P_γ order 0 in this work.

^b“Building-block” operators for the Hamiltonian.

^cSymmetry species in the PI molecular symmetry group G_{12} of 2-methylmalonaldehyde.

^dSymmetry species in the subgroup G_6 , which can be useful when considering matrix elements in the diagonal blocks H_{RR} and H_{LL} in Eq. (1).

Table 3

Symmetry species for various torsional-wagging basis functions

Half-localized tw functions ^a	G_3^b	Delocalized and symmetrized tw functions ^c	G_3^b	G_6^d	G_{12}^e
(R) $\psi(\gamma-\gamma_o)\exp(3k i \alpha)$	A	$[\psi(\gamma-\gamma_o)+\psi(\gamma+\gamma_o)][\exp(3k i \alpha)+\exp(-3k i \alpha)]$	A	A ₁	B ₁
(R) $\psi(\gamma-\gamma_o)\exp[(3k\pm 1)i\alpha]$	E	$[\psi(\gamma-\gamma_o)+\psi(\gamma+\gamma_o)][\exp(3k i \alpha)-\exp(-3k i \alpha)]$	A	A ₂	B ₂
(L) $\psi(\gamma+\gamma_o)\exp(3k i \alpha)$	A	$[\psi(\gamma-\gamma_o)+\psi(\gamma+\gamma_o)] \exp[(3k\pm 1)i\alpha]$	E	E	E ₂
(L) $\psi(\gamma+\gamma_o)\exp[(3k\pm 1)i\alpha]$	E	$[\psi(\gamma-\gamma_o)-\psi(\gamma+\gamma_o)][\exp(3k i \alpha)+\exp(-3k i \alpha)]$	A	A ₁	A ₁
		$[\psi(\gamma-\gamma_o)-\psi(\gamma+\gamma_o)][\exp(3k i \alpha)-\exp(-3k i \alpha)]$	A	A ₂	A ₂
		$[\psi(\gamma-\gamma_o)-\psi(\gamma+\gamma_o)] \exp[(3k\pm 1)i\alpha]$	E	E	E ₁

^aTorsional-wagging functions localized in either the $\gamma = +\gamma_o$ (R) or the $\gamma = -\gamma_o$ (L) region of the schematic potential surface in Fig. 2, but delocalized in the α coordinate. Separate Hamiltonian matrices with the form shown in Eq. (1) are set up for the A and E species basis functions in G_3 .

^bSymmetry species in the group G_3 containing a^2, a^4 , and $a^6 = e$ from Table 1. This is the group used to block-diagonalize the Hamiltonian into separate matrices for A and E species. The E species of G_3 is separably degenerate, though this point is not considered further in this paper.

^cTorsional-wagging basis functions that are delocalized in both the torsional and wagging coordinates. It is sometimes instructive to express eigenfunctions arising after diagonalization of the Hamiltonian matrix in Eq. (1) in terms of these symmetrized basis functions.

^dSymmetry species in the group G_6 , containing the elements $a^2, a^4, a^6 = e$ and a^2b, a^4b, b from Table 1. This group can be used for some symmetry considerations (see Section 4.2) within the diagonal H_{RR} and H_{LL} blocks of Eq. (1). (We assume here that $\psi(-x) = +\psi(x)$, as is appropriate for a Harmonic oscillator ground state wavefunction.)

^eSymmetry species in the group G_{12} , which is the PI molecular symmetry group for 2-MMA and which contains all elements e, a, a^2, a^3, a^4, a^5 and $b, ab, a^2b, a^3b, a^4b, a^5b$ from Table 1. These symmetry species are correct for an odd value of k ; for even k , we must perform the exchange $A \leftrightarrow B$ and $E_1 \leftrightarrow E_2$.

Table 4

Symmetry species for various rotational basis functions

Symmetric-top ^a	G ₃ ^b	G ₆ ^c	G ₁₂ ^d	Asymm-top ^e	G ₃ ^b	G ₆ ^c	G ₁₂ ^d
$ J_e, K_e\rangle + J_e, -K_e\rangle$ ^f	A	A ₁	A ₁	$ J_e, 0, J\rangle$	A	A ₁	A ₁
$ J_e, K_e\rangle - J_e, -K_e\rangle$	A	A ₂	A ₂	$ J_o, 0, J\rangle$	A	A ₂	A ₂
$ J_o, K_e\rangle + J_o, -K_e\rangle$ ^g	A	A ₂	A ₂	$ J, K_{ae}, K_{ce}\rangle$	A	A ₁	A ₁
$ J_o, K_e\rangle - J_o, -K_e\rangle$	A	A ₁	A ₁	$ J, K_{ae}, K_{co}\rangle$	A	A ₂	A ₂
$ J_e, K_o\rangle + J_e, -K_o\rangle$	A	A ₂	B ₂	$ J, K_{ao}, K_{ce}\rangle$	A	A ₁	B ₁
$ J_e, K_o\rangle - J_e, -K_o\rangle$	A	A ₁	B ₁	$ J, K_{ao}, K_{co}\rangle$	A	A ₂	B ₂
$ J_o, K_o\rangle + J_o, -K_o\rangle$	A	A ₁	B ₁				
$ J_o, K_o\rangle - J_o, -K_o\rangle$	A	A ₂	B ₂				

^a Rotational basis functions expressed as sums and differences of symmetric top basis functions.^b Symmetry species in the group G₃ containing a^2 , a^4 , and $a^6 = e$ from Table 1. This is the group used to block-diagonalize the Hamiltonian into separate matrices for A and E species.^c Symmetry species in the group G₆, containing the elements a^2 , a^4 , e and a^2b , a^4b , b from Table 1. This group can be used (with some care, see text) for symmetry considerations within the diagonal H_{RR} and H_{LL} blocks of Eq. (1).^d Symmetry species in the group G₁₂, containing all the elements generated by a and b in Table 1. This group can be used for symmetry considerations in all blocks of Eq. (1).^e Rotational basis functions expressed in $JKaKc$ asymmetric-rotor notation, with e = even and o = odd.^f This row also gives the species for $|J_e, K=0\rangle$.^g This row also gives the species for $|J_o, K=0\rangle$.

Table 5

Molecular parameters obtained from the least-squares fit of 2-MMA-d0 using the hybrid-model program

nlm^a	Operator ^{<i>b,c</i>}	Parameter ^{<i>b,d</i>}	Value ^{<i>e</i>}	
220	P_a^2	F	F	5.48952(69)
	$(1/2)(1-\gamma\cos3\alpha)$	V3	V_3	302.419(47)
211	P_aP_a	RHORHO	ρ	0.0316491(37)
	γP_aP_b	AXG		$-1.342(14)\times10^{-2}$
202	P_a^2	OA	A	0.1676864(20)
	P_b^2	B	B	0.1170827(12)
	P_c^2	C	C	0.06979668(84)
	$\{P_a,P_b\}$	DAB	D_{ab}	0.0013100(44)
422	$(1-\gamma\cos3\alpha)P^2$	FV	F_v	$-2.07(37)\times10^{-5}$
	$(1-\gamma\cos3\alpha)P_a^2$	AK5	k_5	$1.4819(87)\times10^{-3}$
	$(1-\gamma\cos3\alpha)(P_b^2-P_c^2)$	C2	c_2	$-2.283(13)\times10^{-4}$
	$(1-\gamma\cos3\alpha)\{P_a,P_b\}$	ODAB	d_{ab}	$-2.18(11)\times10^{-4}$
413	$P_a\{P_a,(P_b^2-P_c^2)\}$	C4	c_4	$-1.127(15)\times10^{-7}$
	$P_a\{P_a^2,P_b\}$	ODELTA	δ_{ab}	$3.9643(60)\times10^{-7}$
	$\gamma P_aP_bP^2$	AXGJ		$-1.5425(98)\times10^{-7}$
404	$-P^4$	DJ	D_J	$1.07706(15)\times10^{-8}$
	$-P^2P_a^2$	DJK	D_{JK}	$2.2525(23)\times10^{-8}$
	$-P_a^4$	DK	D_K	$1.26266(23)\times10^{-7}$
	$-2P^2(P_b^2-P_c^2)$	ODELN	δ_J	$3.1661(14)\times10^{-9}$
	$-\{P_a^2,(P_b^2-P_c^2)\}$	ODELK	δ_K	$1.2106(45)\times10^{-8}$
000	1	WAG2		-8.77045(38)
211	P_aP_a	WRHO		$-5.580(77)\times10^{-4}$
202	P^2	WAG2J		$6.38(17)\times10^{-5}$
	P_a^2	WAG2K		$6.9575(58)\times10^{-4}$
	$P_b^2-P_c^2$	FWAGBC		$-7.4104(94)\times10^{-5}$
422	$P_a^2P^2$	WGV		$3.53(12)\times10^{-6}$
	$P_a^2P_a^2$	WAK2		$2.751(30)\times10^{-6}$
	$\sin3\alpha\{P_a,P_c\}$	WS3AC		$1.476(32)\times10^{-5}$
413	$P_aP_aP^2$	WALV		$-2.513(74)\times10^{-7}$
404	P^4	WAG2JJ		$-1.633(73)\times10^{-10}$
	$P^2P_a^2$	WAG2JK		$5.26(23)\times10^{-9}$
	P_a^4	WAG2KK		$-2.028(23)\times10^{-8}$
624	$\sin3\alpha\{P_a,P_c\}P^2$	WS3ACJ		$6.55(73)\times10^{-10}$

^aNotation of Ref. 18; $n = l+m$, where n is the total order of the operator, l is the order of the torsional part, and m is the order of the rotational part, respectively; γ is considered to be of order 0.

^b Notation of Refs.¹⁴⁻¹⁵. $\{A,B\} = AB + BA$. The product of the parameter and operator from a given row yields the term actually used in the torsion-rotation-tunneling Hamiltonian, except for F , ρ , and A , which occur in the Hamiltonian in the form $F(P_a - \rho P_a)^2 + AP_a^2$.

^c γ in these operators is shorthand for $\gamma/\langle R|\gamma|R\rangle$, so its matrix elements give only a $\pm$ sign to the final matrix element of the full operator expression. Operators in the upper part of the table have non-zero matrix elements only in the H_{RR} and H_{LL} blocks of Eq. (1); operators in the lower part have non-zero elements only in H_{RL} and H_{LR} .

^d Non-tunneling parameters are first given in the notation of the program, and then in their more usual algebraic notation.

^e Values of the 33 parameters from the fit, with one standard uncertainty (type A, $k=1$ ¹⁹) in parentheses. All parameters are in cm^{-1} , except for ρ , which is unitless. The weighted standard deviation of the fit is 1.03.

Table 6

Molecular parameters obtained from the least-squares fit of 2-MMA-d1 using the hybrid-model program

nlm ^a	Operator ^{b,c}	Parameter ^{b,d}		Value ^e
220	P_a^2	F	F	5.5129(21)
	$(1/2)(1-\gamma\cos 3\alpha)$	V3	V_3	315.36(14)
211	$P_a P_a$	RHORHO	ρ	0.0312528(78)
	$\gamma P_a P_b$	AXG		$-8.006(28) \times 10^{-3}$
202	P_a^2	OA	A	0.1668537(42)
	P_b^2	B	B	0.11496512(24)
	P_c^2	C	C	0.06891734(12)
	$\{P_a, P_b\}$	DAB	D_{ab}	$1.7697(29) \times 10^{-3}$
422	$(1-\gamma\cos 3\alpha)P^2$	FV	F_v	$-7.847(65) \times 10^{-5}$
	$(1-\gamma\cos 3\alpha)P_a^2$	AK5	k_5	$1.325(21) \times 10^{-3}$
	$(1-\gamma\cos 3\alpha)(P_b^2-P_c^2)$	C2	c_2	$-1.4993(63) \times 10^{-4}$
	$(1-\gamma\cos 3\alpha)\{P_a, P_b\}$	ODAB	d_{ab}	$-1.73(13) \times 10^{-4}$
	$\sin 3\alpha\{P_a, P_c\}$	DAC	D_{ac}	$1.915(73) \times 10^{-4}$
413	$\gamma P_a\{P_a^2, P_b\}$	AXGK		$-1.66(12) \times 10^{-6}$
404	$-P^4$	DJ	D_J	$1.02314(11) \times 10^{-8}$
	$-P^2 P_a^2$	DJK	D_{JK}	$2.3582(92) \times 10^{-8}$
	$-P_a^4$	DK	D_K	$1.19954(93) \times 10^{-7}$
	$-2P^2(P_b^2-P_c^2)$	ODELN	δ_J	$2.90540(56) \times 10^{-9}$
	$-\{P_a^2, (P_b^2-P_c^2)\}$	ODELK	δ_K	$1.5269(47) \times 10^{-8}$
	$\{P_a^3, P_b\}$	DABK	D_{abK}	$6.68(37) \times 10^{-8}$
000	1	WAG2		-1.18710(12)
211	$P_a P_a$	WRHO		$-1.463(21) \times 10^{-4}$
202	P^2	WAG2J		$2.8289(79) \times 10^{-6}$
	P_a^2	WAG2K		$1.1585(16) \times 10^{-4}$
	$(P_b^2-P_c^2)$	FWAGBC		$-1.28409(86) \times 10^{-5}$
303	$P_i P_c P^2$	WCPGJ		$6.99(24) \times 10^{-8}$
413	$P_a P_a P^2$	WALV		$-2.37(12) \times 10^{-8}$
	$P_a P_a^3$	WAK1		$5.38(14) \times 10^{-8}$
	$P_a\{P_a, (P_b^2-P_c^2)\}$	WC4		$-1.627(65) \times 10^{-8}$
404	P_a^4	WAG2KK		$-6.22(15) \times 10^{-9}$
	$2P^2(P_b^2-P_c^2)$	FWGBCJ		$7.75(56) \times 10^{-11}$

^a Notation of Ref. 18: $n = l+m$, where n is the total order of the operator, l is the order of the torsional part, and m is the order of the rotational part, respectively; γ is considered to be of order 0.

^b Notation of Refs. 14-15. $\{A, B\} \equiv AB + BA$. The product of the parameter and operator from a given row yields the term actually used in the torsion-rotation-tunneling Hamiltonian, except for F , ρ , and A , which occur in the Hamiltonian in the form $F(P_a - \rho P_a)^2 + AP_a^2$.

^c γ in these operators is shorthand for $\gamma/\langle R|\gamma|R\rangle$, so its matrix elements give only a $\pm$ sign to the final matrix element of the full operator expression. Operators in the upper part of the table have non-zero matrix elements only in the H_{RR} and H_{LL} blocks of Eq. (1); operators in the lower part have non-zero elements only in H_{RL} and H_{LR} .

^d Non-tunneling parameters are given first in the notation of the program, and then in their more usual algebraic notation.

^e Values of the 31 parameters from the fit, with one standard uncertainty (type A, $k=1$ ¹⁹) in parentheses. All parameters are in cm⁻¹, except for ρ , which is unitless. The weighted standard deviation of the fit is 1.11.

Table 7Overview of the 2-MMA-d0 and 2-MMA-d1 fits In Ref.⁹ and in the present work

	2-MMA-d0 ^a			2-MMA-d1 ^b		
	Par. ^c	Lines ^d	σ_{fit} ^e	Par. ^c	Lines ^d	σ_{fit} ^e
Ref. [9]	37	2578	1.03	32	2552	1.08
This work ^f	33	2578	1.03	31	2552	1.11

	Lines ^d	wrms ^g	Lines ^d	wrms ^g
A-species ^f	1322	1.04	1299	1.15
E-species ^f	1256	1.01	1253	1.05

	Lines ^d	rms ^h	Lines ^d	rms ^h
2 kHz lines [9]	176	2.5	–	–
2 kHz lines ^f	176	2.4	–	–
10 kHz lines [9]	1876	11.1	2137	11.5
10 kHz lines ^f	1876	11.1	2137	11.8
50 kHz lines [9]	526	26.3	415	27.5
50 kHz lines ^f	526	26.3	415	27.8

^aThe normal (–OH) isotopic species of 2-methylmalonaldehyde.^bThe isotopolog of 2-MMA with a deuterated hydroxyl group (–OD).^cThe total number of parameters used (and also floated) in the fit.^dThe number of lines in each category included in the fit.^eThe weighted standard deviation of the global fit.^fResults from the present work.^gWeighted root-mean-square residuals for various sub-categories of the lines in the fit. A and E lines indicate transitions within nondegenerate and degenerate torsion-wagging-rotational manifolds, respectively, regardless of their actual symmetry designation in G12. (i.e., A₁, A₂, B₁, B₂ or E₁, E₂)^hRoot-mean square residuals in kHz. The labels 2, 10, and 50 kHz indicate the experimental measurement uncertainty assigned to these subcategories. Because of the D-quadrupole broadening of lines in the 2-MMA-d1 spectrum, 2 kHz uncertainties occur only for the –d0 species.