Tunneling dynamics, symmetry, and far-infrared spectrum of the rotating water trimer. I. Hamiltonian and qualitative model

A. van der Avoird, E. H. T. Olothof, and P. E. S. Wormer
Institute of Theoretical Chemistry, NSR-Center, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

(Received 24 April 1996; accepted 6 August 1996)

A Hamiltonian is derived for the rotating water trimer with three internal motions—the rotations of the monomers about their hydrogen bonds. We obtain an expression of the kinetic energy operator, which is a non-trivial extension of earlier heuristic forms used for the non-rotating trimer. The Coriolis coupling operator between the single-axis monomer angular momenta and the overall trimer rotation is given for the first time. To analyze the effects of the tunneling and Coriolis splittings on the energy levels of the trimer, we introduced a qualitative model for the pseudo-rotation and donor tunneling. By perturbation theory and application of the permutation-inversion groups $G_6$ and $G_{48}$ we obtain algebraic expressions for the splittings due to pseudo-rotation and donor tunneling, respectively. The pseudo-rotation does not produce any internal angular momentum and does not yield first order Coriolis splitting, but in second order the Coriolis coupling lifts various degeneracies and gives rise to observable $J$-dependent splittings. Donor tunneling splits every pseudo-rotation level into a quartet and those levels in this quartet that belong to the three-dimensional irreps of $G_{48}$ into doublets. For $J>0$ a rather complex pattern of larger (for the internal states with $G_6$ labels $k=\pm 1$ and $\pm 2$) and smaller (for the levels with $k=0$ and $k=3$) splittings is obtained, especially for the substates with $|K|=1$ which are Coriolis coupled to the $K=0$ substates. The results of calculations in the companion paper, together with the model introduced in the present paper, will be used to interpret all the tunneling splittings observed in high-resolution spectra of $(H_2O)_3$ and $(D_2O)_3$.

I. INTRODUCTION

Detailed information on the process of hydrogen bond breaking and formation—hydrogen bond network rearrangement (HBNR)—in aqueous systems can be obtained from high-resolution microwave and far-infrared spectra of water clusters in molecular beams.1-4 The dimer has been studied extensively,5-6 but recently the center of attention has shifted to the trimer,1,7-9 while even the spectra of tetrarners, pentamers, and hexamers have now been measured.2-4 The splittings observed in these spectra are explicit manifestations of the HBNR tunneling motions occurring in these clusters: flipping of the non hydrogen-bonded protons between different equilibrium positions, and donor tunneling that involves the breaking and formation of hydrogen bonds.

In the present paper we focus on the tunneling dynamics in the trimer. The cyclic triangular structure found experimentally1 is in agreement with the predictions from earlier ab initio calculations.10,11 The high-resolution far-infrared spectra1,7-9 provide detailed information on the vibration-rotation-tunneling (VRT) dynamics of the water trimer, and have stimulated new theoretical studies. The first step in these studies is to obtain information on the intermolecular potential surface by ab initio electronic structure calculations.12-21 Given the potential surface one can then consider the internal motions occurring in the trimer. The dynamical process that received most attention1,4,13,22-26 is the relatively fast tunneling motion, sometimes called pseudo-rotation or torsion, that corresponds to the flipping of the external protons through the plane of the hydrogen bonded triangular "skeleton" by rotation about the hydrogen bonds. It has been experimentally found,1,7,8 however, that the hydrogen bonds can also break and reconstruct. This is observed in a process, called donor tunneling,2 which involves the interchange of the hydrogen-bonded donor proton of a water monomer with its external proton. Alternatively, this process is called bifurcation tunneling,27 because it proceeds through a transition state in which one of the water monomers donates both its protons in a bifurcated hydrogen bond to its neighboring monomer, or $C_2$ tunneling,24,25 because it may also be viewed as the rotation of a water monomer around its $C_2$ axis—in combination with the flipping of one or both other monomers. Although it is much slower than the pseudo-rotation flipping and leads to much smaller tunneling splittings,1,7,8 some of the theoretical studies have included this donor tunneling. The occurrence of such internal motions in weakly bound and other non-rigid systems can be expressed in terms of "feasible permutations,"1-28 which form the molecular symmetry (MS) or permutation-inversion (PI) group.29 In the case of the water trimer with no mixed isotopes, i.e., for $(H_2O)_3$ and $(D_2O)_3$, it has been established by Liu et al.7 that the PI group associated with the observed tunneling splittings is $G_{48}$.

In all the previous theoretical studies of the water trimer only its internal motions were considered, the overall rotation was not taken into account. In Sec. II we will present the
kinetic energy operator for pseudo-rotation tunneling in a rotating trimer; the derivation of this operator is given in Appendix A. In this derivation we follow the same procedure that we used earlier for van der Waals dimers. We first consider a system where the mass centers of the monomers form a rigid triangle and the molecules are free to rotate in three dimensions around their respective mass centers. Recently, a Hamiltonian was derived in which the mass centers are also free to move. This Hamiltonian is, however, too complicated for our purposes. And indeed, instead of relaxing the rigidity constraint, we impose the additional condition that each monomer can only rotate around the axis which passes through its mass center and its hydrogen-bonded proton.

After discussing the kinetic energy operator, we introduce and elaborate a qualitative semi-empirical/group-theoretical model for the internal motions. We invoke the symmetry group $G_6$ to simplify the description of the pseudo-rotation tunneling. We then augment our model with donor tunneling. In Sec. IV and Appendix C it is shown how the group $G_{48}$ may be helpful in this extension. The effects of Coriolis coupling, in combination with pseudo-rotation and donor tunneling, are analyzed in Sec. V. Some of the more technical aspects, such as the calculation of matrix elements and selection rules, are treated in Appendix B.

In the subsequent paper (paper II) we use the Hamiltonian derived in the present paper (paper I) in quantitative calculations, with two different potentials extracted from ab initio calculations. The results of these calculations will be compared with the experimental spectra, and we will see that the qualitative models of the present paper are very useful for the interpretation of these spectra. We will be able to conclude that all the splittings observed in the high-resolution spectra of $(\text{H}_2\text{O})_3$ and $(\text{D}_2\text{O})_3$—including their dependence on the overall rotation quantum number $J$—can be understood and related to the tunneling motions in these trimers.

II. MODEL HAMILTONIAN FOR PSEUDO-ROTATION TUNNELING

In this section we will introduce the kinetic energy operator of the water trimer that has as the only allowed internal motions the flippings of the "external" hydrogen atoms through the plane of the trimer. Following Refs. 7, 14 and 23 we will refer to this motion as a pseudo-rotation tunneling. The monomers themselves are rigid and their centers of mass form a rigid triangular skeleton. These centers are held together by the "internal"—hydrogen bonding—H atoms. Each monomer is allowed to rotate about one axis, which passes through its center of mass and its hydrogen-bonded proton. The monomer centers of mass are at the points $A$, $B$, and $C$; see Fig. 1. Since our derivations hold also for mixed isotopomers, we denote the monomer masses by different symbols: $M_A$, $M_B$, and $M_C$. The center of mass of the trimer is at point $D$. The atoms in the trimer are labeled by $\nu=A,B,C=1,2,3$ and $i=0,1,2$, for oxygen, hydrogen 1, and hydrogen 2, respectively. The hydrogen 1 atoms are the internal atoms that participate in the hydrogen bonds. In Appendix A we describe the construction of a frame fixed to the trimer. The axis $A-H_{A1}$ makes an angle $\xi_\nu$ with the $x$-axis of this frame. If the trimer skeleton is an equilateral triangle, then the angle $\xi_\nu$ is given by

$$\xi_\nu = \xi_A + (\nu - 1) \frac{2\pi}{3}. \tag{1}$$

We take as a reference geometry the completely planar case in which the angles $\chi_\nu$ are zero; see Fig. 1. In this reference geometry the planes spanned by the monomer principal axes $a$ and $b$ coincide with the plane spanned by the trimer $x$- and $y$-axis. The principal $b$-axis of the monomer $\nu$ makes the angle $\varphi_\nu$ with its rotation axis. In the case of $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$, depicted in Fig. 1, the $b$-axis coincides with the $C_2$-symmetry axis of the monomer.

In Appendix A we derive the kinetic energy operator for our model with the internal coordinates $\chi_A$, $\chi_B$, and $\chi_C$ and the overall rotation. The final result of this Appendix reads

$$T = \frac{1}{2} (J^T - J^I) \mu(\chi)(J - j) + \frac{1}{2} \sum_\nu \Lambda^{-1}_\nu \tilde{p}^I_{\chi_\nu} \tilde{p}_{\chi_\nu}, \tag{2}$$

where

$$\Lambda_\nu = I_x \cos^2 \varphi_\nu + I_y \sin^2 \varphi_\nu. \tag{3}$$

Here $I_x = I_b$, $I_y = I_a$ are inertia moments of water. The operator $J$ is the usual body-fixed form of the rigid rotor angular momentum operator, which is Hermitian, and...
\[ j = \sum j_x, \] where \( j_x \) is given by Eq. (A44) with \( p_{\chi} = -i\hbar \partial / \partial \chi_x \). The latter two operators are non-Hermitian, their Hermitian adjoints are given by Eqs. (A50) and (A49), respectively. So, although Eq. (2) may look familiar, this is deceptive, as may be witnessed from the rather lengthy derivation needed to obtain it.

The effective inertia tensor [Eq. (A37)] is

\[ \mu(\chi)^{-1} = \mathbf{I}_m + \sum_{v} \mathbf{I}_v^{\text{eff}}(\chi_v). \]  

The complicated \( \chi_x \)-dependent terms \( \mathbf{I}_v^{\text{eff}}(\chi_v) \) are smaller than 1% of the term \( \mathbf{I}_m \) and in a first approximation may be neglected. The tensor \( \mathbf{I}_m \) is constant and, for the equilateral triangular structure, it is simply given by Eq. (A16).

In the Coriolis Hamiltonian all kinetic energy terms are collected that are linear in \( \chi_v \). The components of the operator \( \mathbf{J} = \sum j_x \), given by Eq. (A44), are non-Hermitian, even when the weight \( \mu^{1/2}(\chi) \) appearing in the volume element is constant. Although \( j_x \) is not a vector operator, but rather the generator of rotations around a single axis, we will see that it is nevertheless convenient to define the shift operators

\[ \mathbf{j}_z = j_x \pm i j_y. \]  

The Coriolis coupling between the trimer rotation and the three-dimensional pseudo-rotation tunneling has the unusual form

\[ H^{\text{Cor}} = -\frac{1}{2} \mathbf{A} \left[ (j_x^+ + j_x^-) J_x + (j_y^+ + j_y^-) J_y \right] - C (j_z^+ + j_z^-) J_z. \]  

In the evaluation of the matrix elements of \( j_x^\pm \) and \( j_y^\pm \) we will avoid the use of the complicated expression in Eq. (A50) by acting with \( (j_x^\pm)^{\dagger} = j_z \) and \( (j_y^\pm)^{\dagger} = j_z \) on the wave function in the bra.

The operators \( p_{\chi_v} = -i\hbar \partial / \partial \chi_v \) are Hermitian when the weight \( \mu^{1/2}(\chi) = \det[\mu(\chi)]^{-1/2} \) is constant. We assume this to be the case, which is consistent with the neglect of \( \mathbf{I}_v^{\text{eff}}(\chi_v) \) in Eq. (4). Adding the \( \chi_v \)-dependent potential and the \( \mathbf{J} \)-independent terms of Eq. (2), we obtain the Hamiltonian for the internal motions

\[ H^{\text{int}} = -\frac{\hbar^2}{2\Lambda} \sum_{v} \frac{\partial^2}{\partial \chi_v^2} + \frac{1}{2} A (j_x^+ j_x^- + j_y^+ j_y^-) + C j_z j_z + V(\chi_A \cdot \chi_B \cdot \chi_C), \]  

where \( \Lambda = \Lambda_A = \Lambda_B = \Lambda_C \) is given in Eq. (3). The terms that contain the components of \( \mathbf{j} \) arise because the rotations of the external protons are expressed with respect to the moving trimer frame. Obviously, for \( \mathbf{J} = 0 \) only the Hamiltonian (8) needs to be taken into account.

III. PSEUDO-ROTATION TUNNELING AND \( G_6 \) SYMMETRY

We will consider the water trimer with the highest permutational symmetry, that is, \((H_2O)_3\) and \((D_2O)_3\). If needed, it will be straightforward to deduce the effects of the lower symmetry in mixed isotopomers. In order to describe the permutations concisely, it is convenient to relabel the nuclei. The oxygen nuclei \((v, 0)\) of monomers \( v = A, B, C \) are now designated by \( A \), \( B \), and \( C \), and the protons \((v, i)\) with \( i = 1, 2 \) by \{1,2\}, \{3,4\} and \{5,6\}.

The structure of this trimer and the form of the potential \( V(\chi_A, \chi_B, \chi_C) \) in Eq. (8) was obtained from \textit{ab initio} calculations.\(^{11-21}\) All authors agree that the equilibrium structure is non-planar with angles \( \chi_v \) of about \( \pm 50^\circ \). They also agree that there are six equivalent minima in the potential with two positive equilibrium values of \( \chi_v \) and one negative value, and vice-versa. The fixed positions of the oxygen- and \( H_1 \)-nuclei form a rigid planar skeleton and the potential is invariant under those permutations that are in one-to-one correspondence with elements of the point group of this skeleton. When the three centers of mass form an equilateral triangle and \( \xi_v \) obeys Eq. (1), the point group of the skeleton is \( C_3^6 \). In that case the permutation \((ABC)(153)(264)\) and its powers, which permute simultaneously the position vectors of all atoms in monomers \( A \), \( B \), and \( C \), leave \( V(\chi_A, \chi_B, \chi_C) \) invariant. Also \( E^* \), the inversion operation that changes the sign of all position vectors, is then a symmetry operation and the group of feasible permutation-inversion operations is the cyclic group \( G_6 = P(C_3^6) \). This group is generated by \( \mathcal{F} = (ABC)(153)(264) = E^*(ABC) \times (153)(264) \). It is easily verified that \( \mathcal{F} \) is indeed of order 6. The irreps are labeled by \( A_1^+ \), \( A_1^- \), \( A_2 \), \( A_3 \), \( A_3^\dagger \), \( A_5 \) which have the complex characters \( \chi^{(k)}(\mathcal{F})^j = \exp(\pi k n \pi i / 3) \) with \( k = 0,3,-2,1,2,-1 \), respectively.

Let us consider a wave function \( u(\chi_v) \) for monomer \( v \) that is localized above the plane near the minimum in the potential and its counterpart \( d(\chi_v) = u(-\chi_v) \), which is localized below the plane. The functions have sufficient amplitude near \( \chi_v = 0 \) to allow the pseudo-rotation tunneling of the non-hydrogen-bonded protons. The product function \( |u(\chi_A) u(\chi_B) d(\chi_C)| \) is then localized near one of the six equivalent minima in the 3-dimensional potential surface. The action of the group generator \( \mathcal{F} \) on this function yields the function \(|d(-\chi_A) u(-\chi_B) u(-\chi_C)| = |u(\chi_A) d(\chi_B) d(\chi_C)| \), see Appendix B. So, in effect this operation flips the proton of monomer \( B \) from \( u \) to \( d \). The operation may be repeated, each time flipping one of the protons, yielding the functions \( u u d, \mathcal{F} u d = u d, \mathcal{F}^2 u d = d u, \mathcal{F}^3 u d = u u, \) and \( \mathcal{F}^2 u d = d u d \), all six localized near the equivalent global minima in \( V(\chi_A, \chi_B, \chi_C) \). From the \textit{ab initio} calculations follows that the lowest energy barrier occurs between any of the two equilibrium structures that can be reached by the flip of one...
monomer only. The two stationary points in the potential with all monomers up or down, $uuu$ and $ddd$, have a substantially higher energy.

We will use product functions $|\Phi_k\rangle|JKM\rangle$ as a first approximation to the tunneling-rotation states of the water trimer. The "external" function $|JKM\rangle$ is a symmetric top eigenstate, and $|\Phi_k\rangle$ is an "internal" wave function of $G_6$ symmetry. The latter function is located in the six-dimensional model space spanned by basis vectors $\{|\mathcal{F}^n|uud\rangle, n = 0, \ldots, 5\}$. Since each irrep $k$ occurs only once, the symmetry adapted functions

$$|\Phi_k(\chi_A \cdot \chi_B \cdot \chi_C)\rangle = \frac{1}{\sqrt{6}} \sum_{n=-2}^{3} \exp(-nk\pi i/3)|\mathcal{F}^n|u(\chi_A)u(\chi_B)d(\chi_C),$$

$$k = -2, \ldots, 3$$

diagonalize the internal Hamiltonian of Eq. (8) on this space. The energies are given by

$$E_k = \frac{\langle\Phi_k|H^{\text{int}}|\Phi_k\rangle}{\langle\Phi_k|\Phi_k\rangle} = \frac{\sum_{n=-2}^{3} \exp(-nk\pi i/3)(uud|H^{\text{int}}|uud)}{\sum_{n=-2}^{3} \exp(-nk\pi i/3)(uud|uud)}.$$ 

The barriers between the minima in $V(\chi_A \cdot \chi_B \cdot \chi_C)$ are the lowest between the structure $uud$ and its neighboring structures $uud = \mathcal{F}uud$ and $uud = \mathcal{F}^{-1}uud$, in which the protons of one monomer have flipped. Therefore, we may, in first approximation, include only the terms with $n = 0$ and the single-flip terms with $n = \pm 1$. Introducing the matrix elements

$$E^{(0)} = \langle uud|H^{\text{int}}|uud\rangle,$$

$$\beta_1 = \langle uud|H^{\text{int}}|uud\rangle = \langle uud|H^{\text{int}}|dud\rangle,$$

$$S = \langle uud|uud\rangle = \langle uud|dud\rangle = \langle u|d\rangle,$$

we get the energies

$$E_k = E^{(0)} + 2 \cos(k\pi/3)\beta_1.$$

It is apparent from the levels with $J=0$ in Fig. 2 that the level structure is characteristic for a sixfold cyclic system with nearest neighbor interactions. When we neglect the overlap integrals $S$, our result is the same as that of Wales, who made the interesting observation that the result resembles the Hückel molecular orbital levels in benzene. The functions with $k = \pm 1$ and those with $k = \pm 2$ are degenerate, as long as the Coriolis interactions, i.e., the $j-J$ coupling terms in the Hamiltonian of Eq. (2), are neglected. In the quantitative calculations below we will find that the resulting level structure agrees rather well with this simple picture. This is convenient, but not essential, in the ensuing elaboration of our model.

Incidentally, we note that the internal functions $|\{\{\{uuu\} \pm |ddd\}\}|/\sqrt{2}$ with higher energy span the irreps $A_1^+$ and $A_1^-$ with $k = 0$ and $k = 3$.

IV. DONOR TUNNELING AND THE SYMMETRY GROUP $G_{48}$

Donor tunneling is the effect that interchanges the non-hydrogen-bonded proton (or deuteron) in a given water monomer with the hydrogen-bonded proton of the same monomer. The corresponding level splittings have been explicitly observed, and it appears that donor tunneling interferes with the other mechanisms that determine the splitting pattern of the pseudo-rotation levels. Hence we extend our treatment with three additional internal coordinates $t = (t_A, t_B, t_C)$, the donor tunneling coordinates, which we will include in our model wave functions. Since our treatment of this tunneling will be basically semi-empirical and group theoretical, there is no need to explicitly specify these coordinates.

Recalling that we numbered the hydrogen-bonded and non-bonded protons by $2v-1$ and $2v$, respectively, with $v=1,2,3$, we see that proton tunneling is generated by the interchange permutations $(12)$, $(34)$, and $(56)$, although these mere interchanges do not correspond to the lowest energy path for the process. If we extend the group $G_6$ with the eight coset generators $C = E$, $(12)$, $(34)$, $(12)(34)$, $(12)(34)(56)$, and $(12)(34)(56)$, we generate the group $G_{48}$, which is of order 48.

We will find it convenient to write the localized and delocalized model wave functions now as $u(1)u(3)d(5)$ and $\Phi_k(1,3,5)$, where 1 stands for the two relevant coordinates on $A$, i.e., $u(1) = u(\chi_A, t_A)$ and likewise 3 stands for the two coordinates of $B$ and 5 for those of $C$. Subsequently, the 6-dimensional model space is extended to a 48-dimensional space by the action of the coset generators $C$. The Hamiltonian $H^{\text{int}}$ [Eq. (8)] is written as $H^{\text{int}}(1,3,5)$. The diagonalization of $H^{\text{int}}$, corresponding to the relatively fast motion of the angles $\chi_\nu$, was performed with the proton tunnel coor-
coordinates of one of their eight equilibrium conformations. In fact, we could have chosen any of the eight equivalent minima, the energy in Eq. (12) would have been the same. The wave functions corresponding to the different conformations are transformed into one another by the coset generators. We assume that the interaction \( C\Phi_k \) between these different wave functions is negligibly small, which implies that

\[
\langle C^k | H^{(n)} | C\Phi_k \rangle = \delta_{c,c^*} \delta_{k,k} E_k,
\]

where \( E_k \) is the energy of Eq. (12).

The Hamiltonian \( H^{(n)}=H^{(n)}(t_A,t_B,t_C) \) describes the relatively slow donor tunneling; it commutes with all elements of \( G_{48} \). The eight functions \( \{C\Phi_k\} \) span a representation of \( G_{48} \) induced from the irrep \( k \) of \( G_6 \). We can decompose this reducible representation by the use of group theory. Remembering that \( E^* \) is the parity operator, we note that the group \( G_{48} \) is a direct product of a pure permutation group \( G_4\) and the group \( \{E,E^*\} \). Therefore, the irrep labels of \( G_{48} \) are \( \Gamma \) with \( \Gamma \) designating an \( f^2 \)-dimensional \( G_24 \) irrep and \( \pm \) being a parity label.

The group \( G_{24} \) is isomorphic with the point group \( T_h \) and we observe in particular the one to one correspondence between (12)(34)(56) and \( \epsilon \) (the point group inversion operation). We will label the irreps of \( G_{24} \) as is standard for \( T_h \), see, e.g., Ref. 33. Note, however, that the subscripts \( g \) and \( u \) do not pertain to \( E^* \) or \( \epsilon \) (which are not contained in \( G_{24} \)), but to (12)(34)(56). That is, the subscripts \( g \) and \( u \) in the irrep labels are related with the parity of the corresponding states under donor tunneling. We deviate from Ref. 33 by not using the label \( E \) for the real reducible two-dimensional representations, but label its irreducible one-dimensional complex components by \( A_3 \) and \( A_3 \). The group \( G_{24} \) is again a direct product: \( G_{24}=G_{12} \otimes \{E,(12)(34)(56)\} \) and \( G_{12} \) is isomorphic to the tetrahedral point group \( T \). This relatively simple structure of \( G_{48} \) facilitates the group theory considerably.

As is shown in Appendix C, the normalized wave functions adapted to \( G_{48} \) may be written as

\[
\psi_{ij}^{\Gamma^z} = \frac{1}{\sqrt{8}} \sum_k \sum_{n=-2}^3 D_{ij}^{k}(C^{-1}) \Phi_k \exp(-nk \pi i/3) \times C^k \zeta_{1,3,5} \alpha_{(1)} u(1) u(3) d(5),
\]

where Eq. (9) was invoked for \( \Phi_k \). The \( f^T \times f^T \) matrices \( D_{ij}^{k}(C^{-1}) \) are given in Eq. (C2). The functions \( \psi_{ij}^{\Gamma^z} \) with \( i = 1, \ldots, f^T \), span the irrep \( \Gamma^z \) of \( G_{48} \). The spectator index \( j \) must match the \( G_6 \) label \( k \), that is to say, for a given \( \Gamma^z \) and \( j \) there is only one \( k \)-value that yields a non-vanishing result, see Appendix C.

With these fully symmetry adapted wave functions it is easy to evaluate the matrix elements of the Hamiltonian. For the donor tunneling terms we follow Wales' model

\[
\beta_2 = \langle u(1) u(3) d(5) | H^{(n)}(t_A,t_B,t_C) | (34)^* \rangle \times \zeta_{1,3,5} \alpha_{(1)} u(1) u(3) d(5)
\]

and

\[
\beta_3 = \langle u(1) u(3) d(5) | H^{(n)}(t_A,t_B,t_C) | (34)^* \rangle \times \zeta_{1,3,5} \alpha_{(1)} u(1) u(3) d(5).
\]

As we have discussed above, the pseudo-rotation tunneling Hamiltonian \( H^{(n)}(1,3,5) \), cf. Eq. (8), is to a very good approximation diagonal in the present basis. If, in accordance with Ref. 15, we neglect the overlap integrals \( S^2 = |u|d| \), the result \( E_k \) of this contribution is given by Eq. (12). With the donor tunneling matrix elements all vanishing, except those in Eqs. (14) and (15) and with the use of the symmetry properties in Appendix C, we find

\[
\delta_{ij}^{\Gamma^z} E_k + \langle \psi_{ij}^{\Gamma^z} | H^{(n)} | \psi_{ij}^{\Gamma^z} \rangle
\]

\[
= \delta_{ij}^{\Gamma^z} E_k + D_{ij}^{\Gamma^z} [(34)^*] \exp(2k \pi i/3) \beta_2
\]

\[
+ D_{ij}^{\Gamma^z} [(56)] \exp(-k \pi i/3) \beta_2
\]

\[
+ D_{ij}^{\Gamma^z} [(12)] (-1)^k \beta_3.
\]

Here \( k \) matches (\( j, \pm \)) in the sense explained in Appendix C, and also \( j^z \) is associated with a unique \( k \)-value, cf. Eq. (13). For the one-dimensional irreps of \( G_{48} \) the matrices \( D_{ij}^{\Gamma^z} \) are just plus or minus the characters given in Table I. For the three-dimensional irreps \( T^z_g \) and \( T^z_u \) we need only the matrices in Eq. (C2). Notice that in the irrep \( T^z_g \) the matrix elements of (12), (34), and (56) are equal to those of (34)(56), (12)(56), and (12)(34) in the irrep \( T \) of \( G_{12} \), while for \( T^z_u \), they are of opposite sign.

For the one-dimensional irreps this yields directly all the energy levels given in Table II. The three-dimensional irreps \( T^z_g \) and \( T^z_u \) occur more than once in the basis, but if we assume that the pseudo-rotation matrix elements \( \beta_1 \) are much larger than the donor tunneling matrix elements \( \beta_2 \) and \( \beta_3 \)—which is realistic—we may neglect the coupling between the states with different \( E_k \). For the \( E_0 = 2 \beta_1 \) levels and the \( E_3 = -2 \beta_1 \) levels each symmetry occurs only once, and we need just the diagonal matrix elements \( D_{jj}^{\Gamma^z} \) and \( D_{jj}^{\Gamma^z} \). Since these diagonal elements are equal for \( j = 1,2,3 \), cf. Eq. (C2), we can calculate the energy of the \( T^z_g \) and \( T^z_u \).

van der Avoird, Olthof, and Wormer: Rotating water trimer. I
levels with $k=0$ and $k=3$ directly from Eq. (16) with $j'=j=1$. This, again, gives the energies of these levels listed in Table II.

For the $T_u^-$ and $T_g^-$ states with $k=\pm 1$ and the $T_u^+$ and $T_g^+$ states with $k=\pm 2$ the procedure is slightly more complicated. Each of these symmetries occurs twice, see Table II. We illustrate what happens for $k=\pm 1$, where we can construct two basis functions of $T_u^-$ symmetry derived from $\Phi_1$ and $\Phi_{-1}$, respectively. In Eq. (13) we take $j=2$ together with $k=1$ and $j=3$ with $k=-1$, in order to obtain a non-vanishing result. While these functions are non-interacting under $H_{\text{int}}$, they have the same $G_{48}$ symmetry and accordingly they mix under $H_{\text{int}}$. We have to diagonalize a $2 \times 2$ Hamilton matrix, the elements of which are given by Eq. (16) with $j'=2,3$ and $j=2,3$. The diagonal elements are both equal to $E_1-\beta_2/3-\beta_3/3$, the off-diagonal element $(j',j) = (2,3)$ equals $-\exp(2\pi i/3)\delta_1$ with

$$\delta_1 = (2/3)(2\beta_2-\beta_3). (17)$$

It is easily verified that this yields the energies in Table II. For the $k=\pm 1$ levels of $T_u^-$ symmetry and for the $k=\pm 2$ levels of $T_u^+$ and $T_g^+$ symmetry the situation is similar. The matrix elements that are relevant for these levels differ only in the signs of their coefficients of $\beta_2$ and $\beta_3$. So, for the $|k|=1$ levels we find two states of symmetry $T_u^-$ which are split by $-2\delta_1$ and two states of symmetry $T_g^+$ split by

### Table I. Character table of the group $G_{24}^\pm$. The characters of $G_{48}^\pm=\{E,E^\pm\} \otimes G_{24}^\pm$ are obtained by adding a parity label to each irrep and using that the characters of the $+/-$ irreps obtain a $+/-$ sign for the operations with $E^\pm$.\hline
<table>
<thead>
<tr>
<th>$E$</th>
<th>$4,(ACB)$</th>
<th>$4,(ABC)$</th>
<th>$4,(ACB)$</th>
<th>$4,(ABC)$</th>
<th>$3$</th>
<th>$3$</th>
<th>$1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1g}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_{2g}$</td>
<td>1</td>
<td>$-\eta$</td>
<td>$-\eta^*$</td>
<td>$-\eta$</td>
<td>$-\eta^*$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_{3g}$</td>
<td>1</td>
<td>$-\eta^*$</td>
<td>$-\eta$</td>
<td>$-\eta^*$</td>
<td>$-\eta$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$T_u$</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_{1u}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_{2u}$</td>
<td>1</td>
<td>$\eta$</td>
<td>$\eta^*$</td>
<td>$-\eta$</td>
<td>$-\eta^*$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_{3u}$</td>
<td>1</td>
<td>$\eta^*$</td>
<td>$\eta$</td>
<td>$-\eta^*$</td>
<td>$-\eta$</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

*The number of operations in each class is given along with a representative member of that class.

$\eta = \exp(i\pi/3)$. The complex irreps are sometimes denoted as $E_x = A_{2g} \otimes A_{1g}$ and $E_y = A_{2u} \otimes A_{3u}$. \hline

### Table II. Pseudo-rotation flipping and donor tunneling levels for $J=0$, from Eq. (16) in a model according to Wales (Ref. 15). The numbers in parentheses are the nuclear spin statistical weights for (H$_2$O)$_3$ and (D$_2$O)$_3$, respectively, see also Refs. 7 and 43.

<table>
<thead>
<tr>
<th>$G_6$ “flipping”</th>
<th>$G_{48}$ “flipping” and “donor tunneling”</th>
<th>Ab initio $t_1 + t_2 + t_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1g}$ (24,249)</td>
<td>$A_{1g}^\pm$ (1.76)</td>
<td>$2\beta_1 + 2\beta_2 + \beta_3$</td>
</tr>
<tr>
<td>$k=0$</td>
<td>$T_u^\pm$ (3,108)</td>
<td>$2\beta_1 + 2/3\beta_2 + 1/3\beta_3$</td>
</tr>
<tr>
<td></td>
<td>$T_g^\pm$ (9,54)</td>
<td>$2\beta_1 - 2/3\beta_2 - 1/3\beta_3$</td>
</tr>
<tr>
<td></td>
<td>$A_{1u}$ (11,11)</td>
<td>$2\beta_1 - 2\beta_2 - \beta_3$</td>
</tr>
<tr>
<td>$A_{2g}$, $A_{3g}$ (20,240), (20,240)</td>
<td>$A_{2g}^\pm$, $A_{3g}^\pm$ (0.70), (0.70)</td>
<td>$\beta_1 - \beta_2 - \beta_3$</td>
</tr>
<tr>
<td>$k=\pm 1$</td>
<td>$T_u^\pm$ (3,108)</td>
<td>$\beta_1 + \beta_2 - \beta_3$</td>
</tr>
<tr>
<td></td>
<td>$T_g^\pm$ (9,54)</td>
<td>$\beta_1 - 5/3\beta_2 + 1/3\beta_3$</td>
</tr>
<tr>
<td></td>
<td>$A_{2u}$, $A_{3u}$ (8,8), (8,8)</td>
<td>$\beta_1 - \beta_2 + \beta_3$</td>
</tr>
<tr>
<td>$A_{1g}$, $A_{3g}$ (20,240), (20,240)</td>
<td>$A_{1g}^\pm$, $A_{3g}^\pm$ (0.70), (0.70)</td>
<td>$-\beta_1 - \beta_2 + \beta_3$</td>
</tr>
<tr>
<td>$k=\pm 2$</td>
<td>$T_u^\pm$ (3,108)</td>
<td>$-\beta_1 + \beta_2 + \beta_3$</td>
</tr>
<tr>
<td></td>
<td>$T_g^\pm$ (9,54)</td>
<td>$-\beta_1 - 5/3\beta_2 - 1/3\beta_3$</td>
</tr>
<tr>
<td></td>
<td>$A_{1u}$ (11,11)</td>
<td>$-\beta_1 + \beta_2 - \beta_3$</td>
</tr>
<tr>
<td>$A_{1g}$ (24,249)</td>
<td>$A_{1g}^\pm$ (1.76)</td>
<td>$-2\beta_1 + 2\beta_2 + \beta_3$</td>
</tr>
<tr>
<td>$k=3$</td>
<td>$T_u^\pm$ (3,108)</td>
<td>$-2\beta_1 + 2/3\beta_2 - 1/3\beta_3$</td>
</tr>
<tr>
<td></td>
<td>$T_g^\pm$ (9,54)</td>
<td>$-2\beta_1 - 2/3\beta_2 + 1/3\beta_3$</td>
</tr>
<tr>
<td></td>
<td>$A_{1u}$ (11,11)</td>
<td>$-2\beta_1 - 2\beta_2 + \beta_3$</td>
</tr>
</tbody>
</table>
van der Avoird, Olthof, and Wormer: Rotating water trimer. I

For the \( |k| = 2 \) levels we find a doublet of symmetry \( T^z_2 \) and a doublet of symmetry \( T^z_\pm \) split by \( -2\delta_2 \) and \( 2\delta_2 \), respectively, with

\[
\delta_2 = (2/3)(2\beta_2 + \beta_3).
\]  

(18)

This completes the picture of the donor tunneling splittings in the states with \( J = 0 \). In view of our treatment of the Coriolis splitting of the states with \( J > 0 \) in the next section, it is important to emphasize that the donor tunneling induces a coupling between the pseudo-rotation functions \( \Phi_k \) and \( \Phi_{-k} \). This coupling occurs only for the states of symmetry \( T^z_2 \) and \( T^z_\pm \) and it leads to a mixing of the model functions \( \Phi_k \) and \( \Phi_{-k} \) for \( |k| = 1 \) and \( |k| = 2 \).

V. CORIOLIS SPLITTING OF THE PSEUDO-ROTATION AND DONOR TUNNELING LEVELS

We will now introduce \( H^{\text{Cor}} \) [Eq. (7)] as a perturbation and, as stated earlier, we will use the product functions \( \{|\Phi_k\rangle_{JKM}\} \) as zeroth order functions. The corresponding zeroth order Hamiltonian \( H^{\text{int}} + H^{\text{Cor}} \) [Eqs. (8) and (5)] is diagonal in this basis with the energies \( E_k + AJ(J+1) + (C-A)K^2 \). In Appendix B it is shown that the symmetric top function \( |JKM\rangle \) belongs to the irrep \(-K\) of \( G_6 \) and hence the unperturbed states transform according to the \( G_6 \) irrep \( k - K \).

Donor tunneling leads to a small first order splitting of each pseudo-rotation level into a quartet of levels characterized by \( G_{48} \) symmetry labels, see Table II. For the one-dimensional irreps in this quartet the donor tunneling has not much effect on the Coriolis shifts and splittings. They undergo a Coriolis shift that to a very good approximation is equal to the shift of their parent state \( |\Phi_k\rangle \). For the three-dimensional irreps \( T^z_{+1} \) the situation is more involved, because they appear more than once for \( |k| = 1,2 \), but we will see that the same Coriolis matrix elements are needed. The general matrix element required in the perturbation treatment below is

\[
\langle \Phi_k;JK'M'|H^{\text{Cor}}|\Phi_j;JKM\rangle = \sum_{n=-2}^{3} \exp\left[-n(k-K)\pi i/3\right] \times \langle uu'dJK'M'|H^{\text{Cor}}|uu'dJKM\rangle
\]

\[
(19)
\]

with \( k' - K' = k - K \), since \( H^{\text{Cor}} \) is totally symmetric under \( G_6 \). We used here that the action of \( \mathcal{T} \) is defined for internal as well as for external coordinates and that the product function belongs to the irrep \( k - K \) of \( G_6 \). Equation (7) shows that the evaluation of Eq. (19) requires matrix elements of \( j_z \), \( j_z^\dagger \), \( j_\pm \), \( j_\pm^\dagger \) and the corresponding components of the rigid rotor operator \( J \). The latter have the usual effect on the symmetric top function: \( J_x(JKM) = K(K+1) \) and \( J_x(JKM) = [-J(J+1) - K(K+1)]/2J(J+1,K,1,M) \), with \( J_x = J \mp iJ_y \).

The matrix elements of \( j_z \) and \( j_\pm \) over the functions \( \Phi_k \) can be considerably simplified by the use of the \( G_6 \) symmetry. First of all, it is easily shown (see Appendix B) that \( j_z^2 + j_\pm^2 \) is of \( A_1^+ \) symmetry and hence is diagonal in \( k \). Further it is shown in Appendix B that the diagonal elements vanish, hence

\[
\langle \Phi_k|j_z^2 + j_\pm^2|\Phi_{k'}\rangle = 0, \quad \text{for } k,k' = -2,\ldots,3.
\]  

(20)

In other words, the states \( |\Phi_k\rangle \), although called pseudo-rotation states, do not carry any internal angular momentum. This may seem surprising, especially for the degenerate states with \( k = \pm 1 \) and \( \pm 2 \), but it should be remembered that the symmetry label \( k \) represents only the relative phase of the \( u-d \) flips of the monomers in a given wave function \( |\Phi_k\rangle \); it is not the eigenvalue of \( j_z \). The fact that all \( |\Phi_k\rangle \) yield vanishing expectation values of \( j_z^2 + j_\pm^2 \) shows that these flips themselves, which are associated with the rotations of the monomers around their own fixed axes \( h_v \), do not carry any net (vibrational) angular momentum along the trimer \( z \)-axis.

Second, the operators \( j_+ \) and \( j_- \) span the \( A_2^- \) and \( A_3^- \) irreps, respectively. From the cyclic \( G_6 \) symmetry follows easily that the only non-vanishing matrix elements are \( \langle \Phi_{k\pm1}|j_\pm|\Phi_k\rangle \) and \( \langle \Phi_{k\pm2}|j_\pm|\Phi_k\rangle \), so that there is no Coriolis interaction in first order. By introducing the same kinds of approximations that led to the internal energy \( E_k \) [Eq. (12)], we obtain (see Appendix B)

\[
\langle \Phi_{k\pm1}|j_\pm + j_\pm^\dagger|\Phi_k\rangle = 4\exp(\pm 2\pi i/3)\cos[(k\mp 1)\pi i/3]|u|l_\pm|d\rangle,
\]

(21)

where the one-particle operator

\[
l_\pm(\chi) = -i\hbar \exp(\pm i\xi_A)(1 \pm i \cos \chi^t \gamma^t / \partial \gamma),
\]

(22)

arises in the three-particle operator

\[
 j_\pm = \sum_{\nu} \exp[\pm (\nu - 1)2\pi i/3]l_\pm(\chi^\nu),
\]

(23)

cf. Eq. (B5).

Knowing the required matrix elements, we can turn to the effect of Coriolis coupling, which we will consider for the zeroth order states labeled by \( K = 0,\pm 1 \), arbitrary fixed \( J > 0 \), and \( k = 0,\pm 1,\pm 2,3 \). The states with \( |k| = 2,\ldots, J \) are in principle also involved in this coupling, but they give only further shifts, no additional splittings of the levels, and therefore we only consider \( |k| = 1 \). For given \( J,M \) we denote the unperturbed states \( |\Phi_k\rangle_{JKM} \) briefly by \( |k,K,J\rangle \). Since the coupling matrix elements \( -A_2(J,J+x)J_zJ_z|k-1, K-1\rangle \) contain \( A \sim 0.22 \) cm\(^{-1}\), they are about 100 times smaller than the corresponding unperturbed energy differences \( E_k - E_{k-1} \). The same holds for the other Coriolis term \( -A_3 J_zJ_z J_z \). So, we can obtain very good estimates of the energies from second order perturbation theory. We define

\[
 Q_J = -A \exp(2\pi i/3)|u|l_\pm|d\rangle[J(J+1)]^{1/2}.
\]

(24)

From Eq. (21) follows then that the matrix elements are \( Q_J \) and \( Q_J^* \) for the interaction of the states with \( k = 0 \)
and $|k|=1$ and also for the states with $k=3$ and $|k|=2$, while they are $\pm 2|Q|$ and $\pm 2|Q|^*$ for the interaction between states with $|k|=1$ and $|k|=2$.

We first consider shifts and splittings of the levels $k$ corresponding to the one-dimensional irreps of $G_{48}$, i.e., the $A_{1g}, A_{2g}, A_{3g}, A_{1u}, A_{2u}, A_{3u}$ irreps of both parities $\pm$. Evidently, the Euler angles are not affected by proton interchange, which implies that the overall rotation function ($JKM$) is automatically adapted to a definite one-dimensional irrep of $G_{48}$. Hence $|k,K\rangle$ belongs to a one-dimensional irrep of this group. Since $H^{\text{un}}$ does not act on the Euler angles, it is diagonal in $K$ and therefore also in $|k,K\rangle$, and so we can use these product functions as zeroth order functions in the perturbation theory. The perturbation of the degenerate states $|1,1\rangle$ and $|-1,-1\rangle$ must be treated by degenerate second order perturbation theory. This leads to two combination states $(|Q|, 1,1)\pm |Q|^*, |1,-1\rangle)/(|Q|/\sqrt{2})$. The minus combination couples to the $|0,0\rangle$ state with strength $|Q|/\sqrt{2}$ and is shifted upwards in energy, whereas the plus combination does not couple and keeps its unperturbed energy. By the same reasoning we get the $(Q^*, 2,1)\pm |Q^*|-2,1\rangle)/(|Q^*|/\sqrt{2})$ combinations. The minus state couples to the $|3,0\rangle$ level and shifts downwards, the energy of the plus combination is not affected.

The second order Coriolis shifts are summarized in Table III and the resulting level pattern is shown qualitatively in Fig. 2. This pattern is easily derived if one realizes that by Eq. (12) (with $S=0$) $E_1-E_2-E_3=E_0-E_3=|\beta_1|$ and $E_2-E_3$ is twice this value. The most remarkable feature is that in the case of degenerate unperturbed tunneling-rotation levels the degeneracy is lifted. This occurs for the $k=\pm 1$ levels with $K=\pm 1$ which have a fourfold degenerate unperturbed energy; they split into one level with $k-K=0$ that is not shifted with respect to this energy, one level with $k-K=0$ that is raised in energy and a twofold degenerate level with $k-K=\pm 2$ that is lowered. A similar splitting occurs for the fourfold degenerate $k=\pm 2$ levels with $K=\pm 1$; they split into one level with $k-K=3$ that keeps its unperturbed energy, one level with $k-K=3$ that is lowered, and a twofold degenerate level with $k-K=\pm 1$ that is raised in energy. All other levels are shifted as well, but since the Coriolis shifts are much smaller than the rotational energies and no further degeneracies are lifted, these shifts cannot be observed.

We next consider the shifts and splittings of the states of $T_u^+$ and $T_g^-$ symmetry, which occur twice for $|k|=1$ and $|k|=2$, see Table II, and are coupled by the donor tunneling. We have just seen that the external functions ($JKM$) are not affected by donor tunneling, and therefore the states originating from $|k,K\rangle$ and $|-k,K\rangle$ have the same coupling matrix elements as their internal parent states, namely, $\pm \exp(2\pi i/3)\delta$ and $\pm \exp(2\pi i/3)\delta$, for $|k|=1$ and $|k|=2$, respectively, see Sec. IV. Since from our quantitative calculations of $Q_j$ in paper II follows that the first order donor tunneling matrix element has the same order of magnitude as the second order Coriolis interaction, i.e.,

$$
\begin{align*}
\frac{Q_j}{|B_1|} & \approx |\delta_1| \approx |\delta_2|.
\end{align*}
$$

(25)

the resulting level shifts and splittings become rather complex, and are not easily interpreted in terms of perturbation theory. For instance, consider for $|k|=1$ the $|k|=1$ substates of $T_u^+$ and $T_g^-$ symmetry, with parents $|1,1\rangle$, $|-1,1\rangle$, $|1,-1\rangle$, and $|-1,-1\rangle$. The levels with $k-K=0$ and $k-K=\pm 2$ are separated by the Coriolis splitting, cf. Fig. 2. Donor tunneling will lift the remaining degeneracy of the levels with $k-K=\pm 2$ in Fig. 2, and it will also affect substantially the splitting of the levels with $k-K=0$ and the separation between the two sets of levels. Evidently, all the splittings depend on $\delta_{1,2}$, as well as on $Q_j$ and $Q_j^*$. A simi-

| Table III. Coriolis shifts and splittings of the pseudo-rotation tunneling levels for $J>0$. These results apply to the donor tunneling states that correspond to the irreps $A_{1g}, A_{2g}, A_{3g}, A_{1u}, A_{2u}, A_{3u}$ of $G_{48}$.

<table>
<thead>
<tr>
<th>$k$</th>
<th>$K$</th>
<th>Unperturbed energy$^a$</th>
<th>$k-K$</th>
<th>Shift$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$\pm 1$</td>
<td>$E_0-A+C$</td>
<td>$\pm 1$</td>
<td>$</td>
</tr>
<tr>
<td>0</td>
<td>$\pm 1$</td>
<td>$E_1-A+C$</td>
<td>$\pm 2$</td>
<td>$4</td>
</tr>
<tr>
<td>0</td>
<td>$\pm 1$</td>
<td>$E_2-A+C$</td>
<td>$\pm 1$</td>
<td>$2</td>
</tr>
<tr>
<td>3</td>
<td>$\pm 1$</td>
<td>$E_3-A+C$</td>
<td>$\pm 2$</td>
<td>$4</td>
</tr>
<tr>
<td>0</td>
<td>$\pm 1$</td>
<td>$E_4-A+C$</td>
<td>$\pm 2$</td>
<td>$2</td>
</tr>
</tbody>
</table>

$^a$The rotational energy contribution $AJ(J+1)$ and the donor tunneling energies (see Table II) must still be added to this energy.

$^b$Note that the small (less than 1%) contribution $A-C$ to the energy differences in the denominators has been neglected and that $|Q|^2 = A^2 [(u|l, d)|^2 J(J+1)$. 

FIG. 3. Qualitative picture of the pseudo-rotation tunneling levels of the water trimer. The corresponding quantitative results are given in Table IV of paper II. This pattern occurs for each of the donor tunneling states that belong to the irreps $T_u^u$ and $T_g^u$ of $G_{48}$. Note that the levels can no longer be labeled by the quantum number $k - K$. The donor tunneling splittings are not shown, except for the splittings due to the interaction of the states with the same $G_{48}$ symmetry. The arrows indicate the splittings $2\delta_1$ and $2\delta_2$.

The $K = 0$ levels with $|k| = 1$ and $|k| = 2$ behave much more regularly. The $T_u^u$ and $T_g^u$ substates of these levels are simply split by donor tunneling by the amounts $2\delta_1$ and $2\delta_2$, just as the corresponding states for $J = 0$, see Fig. 3.

Also the internal levels with $k = 0$ and $k = 3$ are split into a quartet of levels, among which are the levels of $T_u^u$ and $T_g^u$ symmetry. It seems at first sight that here the situation is simpler, because these three-dimensional $G_{48}$ irreps occur just once for these $k$ values, see Table II. For $J = 0$ the internal $k = 0$ and $k = 3$ states are indeed not affected by donor tunneling, apart from their first order splitting into a quartet.

For $J > 0$ there is of course the rotational splitting from the zeroth order term $(C - A)K^2$, shown for $K = 0$ and $K = \pm 1$ in Fig. 2. It is remarkable, however, that also the degeneracy of the $k = 0$ and $k = 3$ levels with $K = \pm 1$ is lifted. This splitting, although reminiscent of $K$-type doubling, is not due to asymmetry of the rotor, but, as we will see, to the combined effect of Coriolis interaction and donor tunneling. It is a very small effect, but we cannot avoid discussing it if we wish to interpret the experimental spectrum (see paper II).

In this paper we have rigorously derived the Hamiltonian of our quantitative calculations in paper II, and for the interpretation of the various splittings observed in the high-resolution spectra. Much of the ambiguity in the assignment of these spectra can thus be removed, and all the inter-

VI. CONCLUSION

In this paper we have rigorously derived the Hamiltonian for the constrained monomer rotations or torsions associated with pseudo-rotation tunneling, in a rotating water trimer. It includes the kinetic energy operator used in earlier calculations; our derivation yields an explicit expression for the effective monomer moments of inertia. But, even for $J = 0$, it also includes other terms which contain the operator $j$, the vector sum of the angular momenta associated with the fixed-axis rotations of the monomers. Note that this operator is non-Hermitian; the expression for the Hamiltonian adopts a simple form only when it is written in terms of $j$ and $j^\dagger$. Furthermore, our derivation yields the explicit form of the Coriolis coupling operator between the internal and overall trimer rotations. Also this operator contains the components of $j$ and $j^\dagger$, and, of course, the total angular momentum $J$.

Next we have introduced a simple model for the pseudo-rotation and donor tunneling. It is shown that, by the use of group theory—with the symmetry group $G_{48}$ if only pseudo-rotation occurs, and the group $G_{48}$ if donor tunneling is allowed as well—the splittings that result from both these tunneling motions can be given algebraically. For $J = 0$ our model results are very similar to those of Wales. For a rotating trimer with $J > 0$ there are important Coriolis coupling effects. It turns out, as explained below Eq. (20), but contrary to expectations, that the pseudo-rotation does not produce any internal (vibrational) angular momentum. Hence, there is no first order Coriolis splitting. In second order, the Coriolis coupling lifts various degeneracies and, thereby, gives rise to observable $J$-dependent splittings. Donor tunneling splits every pseudo-rotation level into a quartet and, in addition, splits the levels in this quartet that belong to the three-dimensional irreps of $G_{48}$ further into doublets. For $J = 0$ this doublet splitting occurs only for the pseudo-rotation states with $G_6$ irrep labels equal to $K = \pm 1$ and $k = \pm 2$. Group theory tells us that this is a consequence of the fact that each of these pseudo-rotation levels has two substates that induce to the same three-dimensional $G_{48}$ irrep. For $J > 0$ and $|K| = 1$ even the pseudo-rotation states with $k = 0$ and $k = 3$ are split into doublets for the three-dimensional $G_{48}$ irreps, through Coriolis mixing with the $G_6$ and $G_8$ states.

The resulting eigenstates are combinations of the Coriolis perturbed wave functions, and the corresponding eigenvalues are split by $2|Q_j|^2\delta_j/(E_1 - E_0)^2$. Since the Coriolis coupling constant $Q_j$ is proportional to $[J(J + 1)]^{1/2}$, cf. Eq. (24), the splitting of the levels with $k = 0$ and $K = \pm 1$ is proportional to $J(J + 1)$. The levels with $k = 3$ and $K = \pm 1$ are split by a similar mechanism. They acquire a donor tunneling splitting $2|Q_j|^2\delta_j/(E_1 - E_0)^2$, which is proportional to $J(J + 1)$, by admixture of the $|\pm 2, 0\rangle$ states. All the degeneracies of the $T_u^u$ and $T_g^u$ levels are now lifted, see Fig. 3.
A9: KINETIC ENERGY OPERATOR

In this Appendix we will derive the kinetic energy operator of the water trimer with the constraints described in the main text. Following Podolsky,38 we will express the kinetic energy in terms of the Laplace operator in generalized coordinates \( q \), i.e., we write

\[
2T = g^{1/2} p^T g^{1/2} G^{-1} p,
\]

where \( p \) are the momenta conjugate to \( q \) and \( g \) is the determinant of the metric tensor \( G \). The metric tensor \( G \) associated with the coordinates \( q \) will be obtained from the classical kinetic energy \( 2T = \dot{q}(t) ^T G \dot{q}(t) \), where the dot indicates the time derivative \( d/dt \).

Before starting the derivations, we wish to point out that it is often convenient to write \( x \times r = Xr \), that is, to express the vector product by means of the antisymmetric matrix

\[
X = \begin{pmatrix} 0 & -z & y \\ z & 0 & -x \\ -y & x & 0 \end{pmatrix}, \text{ where } \begin{pmatrix} x \\ y \\ z \end{pmatrix} = x. \tag{A2}
\]

First we will briefly outline the procedure for a somewhat less constrained system that consists of three rigid water molecules freely rotating around their respective centers of mass, but with these centers forming a rigid triangle. Then we will consider the case that each monomer rotates around a fixed axis.

1. General monomer rotations

We define a right-handed frame fixed to the trimer with the mass centers \( A, B, \) and \( C \) in the \( xy \)-plane. The \( x \)-axis of this frame is \( \vec{f}_x = N_x (2DA - DB - DC) \), with the normalization constant \( N_x \) chosen such that this vector has unit length. (See Fig. 1 for the definition of the vector \( DX \), pointing from \( D \) to \( X \), \( X = A, B, C \).) If the monomer mass centers form an equilateral triangle, the direction of the \( y \)-axis can be defined by the vector \( \vec{f}_y = N_y (DB - DC) \), with the normalization constant \( N_y \). If the structure is less symmetric we must orthogonalize \( \vec{f}_x \) and \( \vec{f}_y \). The vector \( \vec{f}_z \) is simply \( \vec{f}_x \times \vec{f}_y \). This frame is expressed with respect to a laboratory fixed frame \( e = (e_x, e_y, e_z) \) by the Euler rotation

\[
\vec{f} = e \mathbf{R}_{zy} (\alpha, \beta, \gamma), \tag{A3}
\]

with \( R_{zy} (\alpha, \beta, \gamma) = R_z(\alpha) R_y(\beta) R_z(\gamma) \) and the rotation matrices are defined by the active rotation convention, e.g.,

\[
R_z(\alpha) = \begin{pmatrix} \cos \alpha & -\sin \alpha & 0 \\ \sin \alpha & \cos \alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{A4}
\]

The matrix \( R_y(\beta) \) is defined analogously.

Using the atom numbering introduced in the main text, we can express the position vector of each atom relative to the center of mass of the trimer as

\[
\vec{D} \vec{v}_{r,i} = \vec{f} \mathbf{R}_{zy} (\alpha, \beta, \gamma) \vec{v}_{r,i}.
\]

The atomic masses are \( m_{r,i} \) and the kinetic energy (without the overall translation energy) of the system is35

\[
2T = \omega^T A \omega + \sum_{r,i} m_{r,i} |\vec{d}_{r,i}|^2 + 2 \omega^T \sum_{r,i} m_{r,i} \vec{d}_{r,i} \times \vec{d}_{r,i}.
\]

Here the inertia tensor \( A = \sum_{r,i} m_{r,i} D_{r,i}^T D_{r,i} \), where the antisymmetric matrices \( D_{r,i} \) are constructed from the position vectors \( \vec{d}_{r,i} \) as in Eq. (A2). The angular velocity \( \omega \) is related linearly to the time derivatives of the Euler angles

\[
\omega = N \begin{pmatrix} \dot{\alpha} \\ \dot{\beta} \\ \dot{\gamma} \end{pmatrix} \quad \text{with} \quad N = \begin{pmatrix} -\cos \gamma & \sin \gamma & 0 \\ \sin \beta \sin \gamma & \sin \beta \cos \gamma & 0 \\ \cos \beta \cos \gamma & -\cos \beta \sin \gamma & \sin \beta \end{pmatrix}. \tag{A7}
\]

For future use we give \( N^{-1} \)

\[
N^{-1} = \frac{1}{\sin \beta} \begin{pmatrix} -\cos \gamma & \sin \gamma & 0 \\ \sin \beta \sin \gamma & \sin \beta \cos \gamma & 0 \\ \cos \beta \cos \gamma & -\cos \beta \sin \gamma & \sin \beta \end{pmatrix}.
\]

We shall now introduce the constraint that the position vectors \( DA, DB, \) and \( DC \) of the monomer mass centers have constant coordinates \( v_i \), relative to the trimer frame, see Fig. 1. Further we take the monomers to be rigid, which means that the coordinate vector \( x_{r,i} \) of atom \( r,i \), defined relative to the principal axes frame of monomer \( r \), is not dependent on the time \( t \). The monomer Euler angles \( \xi_r(t) \) describe the rotation of the principal axes frame of monomer \( r \) with respect to the trimer frame, similar as in Eq. (A3). These angles and the corresponding angular velocities \( \omega_r \) are

\[
\xi_r(t) = \begin{pmatrix} \alpha_r(t) \\ \beta_r(t) \\ \gamma_r(t) \end{pmatrix} \quad \text{and} \quad \omega_r = N_r \begin{pmatrix} \dot{\alpha}_r \\ \dot{\beta}_r \\ \dot{\gamma}_r \end{pmatrix}. \tag{A9}
\]

The matrices \( N_r \) are given in terms of the angles \( \xi_r \) by equations analogous to Eq. (A8). The position vector \( d_{r,i}(t) \) becomes

\[
d_{r,i}(t) = v_i + R_{zy} (\xi_r(t)) \vec{x}_{r,i}.
\]

By elementary rigid rotor theory36 we obtain

\[
\dot{d}_{r,i} = R_{zy} (\xi_r(t)) \omega_r \times \vec{x}_{r,i}.
\]

When we write this by the use of Eq. (A2) as

\[
\dot{d}_{r,i} = -R_{zy} (\xi_r(t)) \vec{x}_{r,i} \omega_r,
\]

it follows immediately that
\[ \sum_{v} m_{v,i} |d_{v,i}|^2 = \omega^T I_{v} \omega_{v} \tag{A13} \]

where \( I_{v} = \sum_{v} m_{v,i} X_{v,i} X_{v,i} \) is the inertia tensor of monomer \( v \). This tensor is diagonal because it is expressed with respect to the principal axes frame of \( v \). The quantity \( \sum_{v} m_{v,i} X_{v,i} \) arising in the Coriolis, i.e., the last, term of Eq. (A6), is the angular momentum associated with the internal rotation of water monomer \( v \). This vector becomes, since \( 2\omega = 0 \),

\[ j_{\text{int}} = R_{22} (\zeta_v) I_{v} \omega_{v} \tag{A14} \]

Before completing the expression for the classical kinetic energy, we return to the overall inertia tensor of the trimer \( A = \sum_{v} m_{v,i} D_{v,i} D_{v,i} \). By substitution of Eq. (A10) for the vectors \( d_{v,i}(t) \) and the use of \( \sum_{v} m_{v,i} = M_{v} \), we find for the overall inertia tensor

\[ A = \sum_{v} M_{v} V_{v}^T V_{v} + \sum_{v} m_{v,i} R_{22} (\zeta_v) \sum_{v} X_{v,i} X_{v,i} R_{22} (\zeta_v)^T \]

\[ = I_{M} + \sum_{v} R_{22} (\zeta_v) I_{v} R_{22} (\zeta_v)^T \tag{A15} \]

This is Steiner’s theorem for the displacement of an inertia tensor. The antisymmetric matrices \( V_{v} \) correspond to the position vectors \( v_v \) of the monomer centers of mass.

Note parenthetically that in the special case of the equilibrium structure being an equilateral triangle with distance \( R \) between these mass centers and the monomers having equal masses \( M_{v} = M \), the first term \( I_{M} \) of the inertia tensor is simply

\[ I_{M} = \frac{1}{2} MR^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \tag{A16} \]

Recalling that the Coriolis term is \( 2 \omega^T \sum_{v} j_{\text{int}}^{\text{int}} \) and using Eq. (A14) for \( j_{\text{int}}^{\text{int}} \), we find that the kinetic energy is

\[ 2T = \omega^T A \omega + \sum_{v} \omega^T I_{v} \omega_{v} + 2 \omega^T \sum_{v} R_{22} (\zeta_v) I_{v} \omega_{v} \tag{A17} \]

In matrix form the kinetic energy may be written with the use of Eqs. (A7), (A9), and the definition

\[ B_{v} = R_{22} (\zeta_v) I_{v} \tag{A18} \]

as

\[ 2T = \begin{pmatrix} \xi \\ \xi_a \\ \xi_b \\ \xi_c \end{pmatrix}^T \begin{pmatrix} N_T & 0 & 0 & 0 \\ 0 & N_A & 0 & 0 \\ 0 & 0 & N_B & 0 \\ 0 & 0 & 0 & N_C \end{pmatrix} \begin{pmatrix} \xi \\ \xi_a \\ \xi_b \\ \xi_c \end{pmatrix} \times \begin{pmatrix} A & B_A & B_B & B_C \\ B_A^T & I_A & 0 & 0 \\ B_B^T & 0 & I_B & 0 \\ B_C^T & 0 & 0 & I_C \end{pmatrix} \begin{pmatrix} N & 0 & 0 & 0 \\ 0 & N_A & 0 & 0 \\ 0 & 0 & N_B & 0 \\ 0 & 0 & 0 & N_C \end{pmatrix} \tag{A19} \]

We recognize the Lagrange form of the kinetic energy \( 2T \) with the four sets of Euler angles playing the role of the generalized coordinates \( q \). This equation defines the metric tensor \( G \). To obtain the corresponding quantum mechanical operator we must write the classical expression in Hamilton form, \( 2T = p^T G^{-1} p \), with the generalized momenta \( p = Gq \). For the inversion of the metric tensor \( G \) we can use the Frobenius formula, \( G_{ij} = \sum_k G_{ik} G_{kj} \), which we repeat here for the convenience of the reader

\[ \begin{pmatrix} M_{11} & M_{12} & - \mu M_{12} M_{22}^{-1} \\ M_{21} & M_{22} & - \mu M_{12} M_{22}^{-1} \\ -\mu M_{12} M_{22}^{-1} & -\mu M_{12} M_{22}^{-1} & M_{12} M_{22}^{-1} + M_{22}^{-1} \end{pmatrix} \tag{A20} \]

with \( \mu^{-1} = M_{11}^{-1} - M_{12} M_{22}^{-1} M_{21} \). In this case we partition the middle factor of \( G \) so that \( M_{11} = A \). The effective inertia tensor becomes

\[ \mu^{-1} = A - \sum_{v} B_{v} J_{v}^{-1} B_{v}^T \tag{A21} \]

With the use of Eqs. (A15) and (A18) we obtain simply \( \mu^{-1} = I_{M} \). We observe that all terms associated with the monomer rotations cancel; the effective inertia tensor is simply the constant tensor \( I_{M} \) that corresponds to the monomers being point masses \( M_{v} \) at fixed positions \( v \). This tensor is easily inverted.

The momenta \( p_{\xi} \) and \( p_{\zeta} \) are conjugate to the angular coordinates \( \xi \) and \( \zeta \); the associated classical angular momenta are defined by

\[ J = N^{-1} p_{\xi} \quad \text{and} \quad \jmath_{v} = N_{v}^{-1} p_{\zeta_{v}} \tag{A22} \]

where \( \jmath_{v} \) is with respect to the principal axes frame of monomer \( v \). The total angular momentum with respect to the trimer frame is
\[ j = \sum_{\nu} R_{\nu}(\xi_{\nu}) j_{\nu}. \quad (A23) \]

In terms of the angular momenta the classical kinetic energy becomes

\[ 2T = (J^T - j^T)I_{\nu}^{-1}(J - j) + \sum_{\nu} j_{\nu}^0 I_{\nu}^{-1} j_{\nu}. \quad (A24) \]

This result is easily quantized. We must replace the momenta by the gradient operators

\[ p_{\xi_{\nu}} = -i\hbar \left( \begin{array}{c} \partial \partial \alpha \\ \partial \partial \beta \\ \partial \partial \gamma \end{array} \right), \quad (A25) \]

and similarly for \( \xi_{\nu} \). The total angular momentum becomes

\[ J = -i\hbar N^{-1T} \left( \begin{array}{c} \partial \partial \alpha \\ \partial \partial \beta \\ \partial \partial \gamma \end{array} \right), \quad (A26) \]

which is the standard form of this operator in a body-fixed frame, [cf. Eq. (A8)], that satisfies the well-known anomalous commutation relations

\[ [J_x, J_y] = -i\hbar J_z, \quad \text{etc.} \quad (A27) \]

As follows from Eq. (A22), \( j_{\nu} \) has the standard form of an operator expressed with respect to a BF frame. The effective inertia tensor \( I_{\nu} \) and the monomer inertia tensors \( I_{\nu} \) are constant and, moreover, the latter are diagonal. The volume element \( g^{1/2} \) appears in the expression of the Laplace operator in generalized coordinates, cf. Eq. (A1). Here \( g = \det(G) \) contains only constant factors and the usual factors \( \sin \beta \) and \( \sin \beta \). Since the total and the monomer angular momentum operators are Hermitian and satisfy the usual commutation relations, the quantized form of the kinetic energy has the same simple appearance as the classical form in Eq. (A24). This concludes the case of the freely rotating water molecules.

2. Single axis monomer rotations

We now turn to the case that the water molecules are allowed to rotate only about \( \bar{X}H_{v,1} \), and introduce the unit vectors \( h_{\nu} \) by

\[ \bar{X}H_{v,1} = \bar{f} h_{\nu}, \quad X = A, B, C \quad \text{for} \quad \nu = 1, 2, 3, \quad |h_{\nu}| = 1, \quad (A28) \]

see Fig. 1. The theory above must be modified on three accounts. In the first place it is more convenient to apply the \( (h, \chi) \) parametrization of the rotations, rather than the Euler parametrization. The analogue of \( R_{xy}(\xi(t)) \) is

\[ R(h_{\nu}, \chi(t)) = 1 + \sin \chi(t)H_{\nu} + (1 - \cos \chi(t))H_{\nu}^2. \quad (A29) \]

with \( 1 \) being the \( 3 \times 3 \) unit matrix and the antisymmetric matrix \( H_{\nu} \) corresponding to the vector \( h_{\nu} \).

Second, since there is now one degree of freedom per monomer, the angular velocity in Eq. (A9) becomes \( \omega_{\nu} = h_{\nu} \chi_{\nu} \). Also only one column \( \mathbf{b}_{\nu} \) must be included of each of the \( (h, \chi) \) analogs of the matrices \( B_{\nu} \), cf. Eq. (A18).

In the third place, as discussed in the main text, we do not have a reference geometry in which the principal axes of the monomers are parallel to the trimer frame. The principal \( b \)-axis of the monomer \( \nu \) makes the angle \( \varphi_{\nu} \) with the rotation axis \( h_{\nu} \). The component of \( h_{\nu} \) along \( f_{\nu} \) is \( \cos \xi_{\nu} \), see Fig. 1. The analogue of Eq. (A10) reads therefore

\[ d_{\nu,i}(t) = v_{\nu} + R(h_{\nu}, \chi_{\nu}(t))x_{\nu,i}(0) \]

with

\[ x_{\nu,i}(0) = R_{\nu}(\xi_{\nu} - \varphi_{\nu})x_{\nu,i}, \quad (A30) \]

where, as before, \( x_{\nu,i} \) is the coordinate of particle \( i \) expressed with respect to the principal axes of \( \nu \).

The first term of the kinetic energy (A17) is unaffected and the second becomes \( \Lambda_{\nu} \chi_\nu^2 \), instead of Eq. (A13), with \( \Lambda_{\nu} = \hbar^2 I_{\nu}(\chi_{\nu})h_{\nu} \). Here we have introduced the instantaneous inertia tensor of monomer \( \nu \)

\[ I_{\nu}(\chi_{\nu}) = R(h_{\nu}, \chi_{\nu})I_{\nu}(0)R^T(h_{\nu}, \chi_{\nu}). \quad (A31) \]

with its components expressed with respect to the trimer frame. The inertia tensor of monomer \( \nu \) in the reference geometry is given by \( I_{\nu}(0) = \sum_i m_{\nu,i}X_{\nu,i}^T(0)X_{\nu,i}(0) \). This tensor is connected with the diagonal inertia tensor \( I_{\nu} \) of this monomer via

\[ I_{\nu}(0) = R_{\nu}(\xi_{\nu} - \varphi_{\nu})I_{\nu}(0)R_{\nu}^T(\xi_{\nu} - \varphi_{\nu}). \quad (A32) \]

The third (Coriolis) term of Eq. (A17) is now

\[ 2\omega_{\nu} \sum_{\nu} R(h_{\nu}, \chi_{\nu})I_{\nu}(0)h_{\nu}\chi_{\nu} = 2\omega_{\nu} \sum_{\nu} b_{\nu} \dot{\chi}_{\nu}. \quad (A33) \]

Evidently, the vector \( b_{\nu} \), thus defined, depends on \( \chi_{\nu} \). In fact, this vector is the analogue of the matrix \( B_{\nu} \), Eq. (A18). We define the matrix \( B = (b_A, b_B, b_C) \) with the column vectors \( b_{\nu} \) and also

\[ \Lambda = \left( \begin{array}{ccc} \Lambda_A & 0 & 0 \\
0 & \Lambda_B & 0 \\
0 & 0 & \Lambda_C \end{array} \right) \quad \text{and} \quad \dot{\chi} = \left( \begin{array}{c} \dot{\chi}_A \\
\dot{\chi}_B \\
\dot{\chi}_C \end{array} \right). \quad (A34) \]

The kinetic energy in Eq. (A17) becomes the equivalent of Eq. (A19)

\[ 2T = (\dot{\xi}^T, \dot{\chi}^T) \left( \begin{array}{cc} N^T & 0 \\
0 & 1 \end{array} \right) \left( \begin{array}{cc} A & B \\
B^T & \Lambda \end{array} \right) \left( \begin{array}{cc} N & 0 \\
0 & 1 \end{array} \right) \dot{\xi}. \quad (A35) \]

where we used, as before, Eq. (A7) to express the angular velocity of the trimer frame \( \omega \) in terms of the time derivative of its Euler angles \( \dot{\xi} \). This expression contains again the metric tensor \( G \) and, in order to transform \( 2T \) to the Hamilton formalism, we must invert it. By the use of Eq. (A20)
\[
\begin{pmatrix}
A & B \\
B^T & \Lambda
\end{pmatrix}^{-1} = \begin{pmatrix}
\mu & -\mu B \Lambda^{-1} \\
-\Lambda^{-1} B^T \mu & \Lambda^{-1} B^T \mu B \Lambda^{-1} + \Lambda^{-1}
\end{pmatrix},
\]
with \(\mu = (A - B \Lambda^{-1} B^T)^{-1}\). Whereas previously \(\mu\) simplified drastically by the cancellation of terms, this does not occur here. The effective inertia tensor is more complicated than in the system with freely rotating monomers. Using Eq. (A15) we get
\[
\mu(\chi)^{-1} = I_M + \sum \mu^\text{eff}(x_n)
\]
with
\[
\mu^\text{eff}(x_n) = I_n(x_n) - A^{-1} B^T A^{-1}.
\]

The monomer tensor \(\mu^\text{eff}(x_n)\) can be expressed in different ways by the use of Eqs. (A31) and (A32). Evidently, \(\mu^\text{eff}(x_n)\) also depends on the fixed angles \(\varphi_n\) and \(\chi_n\). Also \(\Lambda_n\) can be written in different forms. For instance, observing that
\[
\frac{1}{2} = \left(\begin{array}{c}
1 \\
0 \\
0
\end{array}\right) \quad \text{with} \quad \frac{1}{2} = \left(\begin{array}{c}
1 \\
0 \\
0
\end{array}\right)
\]
we have
\[
\Lambda_n = h_n^T I_n(x_n) h_n = h_n^T I_n(0) h_n = e_n^T R_n(\varphi_n) I_n(\varphi_n) e_n
\]
If we introduce
\[
I_n' = R_n(\varphi_n) I_n R_n(\varphi_n),
\]
we find simply that \(\Lambda_n = (I_n')_{xx}\).

From the implicit definition of the \(G\) tensor in Eq. (A35) it follows that the momenta conjugate to \(\xi\) and \(\chi\), respectively, are:
\[
p_{\xi} = N^T A \xi + N^T B \chi
\]
\[
p_{\chi} = B^T N \xi + A \chi.
\]
We write the total angular momentum again as in Eq. (A22), i.e., \(J = N^{-1} p_{\xi}\), and the angular momentum of monomer \(v\) associated with the rotations about the fixed axis \(h_v\) as
\[
j_v = \Lambda_n^{-1} b_v p_{\chi_v}.
\]
We will need an explicit expression for \(j_v\). In the column vector \(b_v = R(h_v, \chi_v) I_n(0) h_v\), see Eq. (A33), the following relation:
\[
R(h_v, \chi_v) = R_v(\xi_v) R(e_v, \chi_v) R_v(- \xi_v)
\]
can be used with, of course, \(R(e_v, \chi_v) = R_v(\chi_v)\). If one then substitutes Eqs. (A32) and (A40) \(j_v\) obtains the following form:
\[
j_v = \begin{pmatrix}
\cos \xi_v - \cos \chi_v \sin \xi_v (I_v')_{xx} / (I_v')_{xx} \\
\sin \xi_v - \cos \chi_v \cos \xi_v (I_v')_{xx} / (I_v')_{xx} \\
\chi_v (I_v')_{xx} (I_v')_{xx}
\end{pmatrix} p_{\chi_v},
\]
with
\[
(I_v')_{xx} = (I_v)^{0.5} \cos \varphi_v + (I_v)^{0.5} \sin \varphi_v
\]
\[
(I_v')_{xx} = [(I_v)^{0.5} - (I_v)^{0.5}] \sin \varphi_v \cos \varphi_v.
\]

The classical kinetic energy becomes then
\[
2T = (J - j)^T \mu (J - j) + p_{\chi}^T \Lambda^{-1} p_{\chi}.
\]

When quantizing we must replace the momenta by gradient operators (times \(-i\hbar\)). The overall angular momentum becomes the same as in Eq. (A26). The monomer operator \(J_v\) obtains the form of Eq. (A45) with \(p_{\chi_v}\) replaced by \(-i\hbar \partial / \partial \chi_v\). The volume element associated with generalized coordinates is \(|g|^{1/2} \Pi_i dq_i\), where \(g\) is the determinant of the metric tensor \(G\). The weight \(|g|^{1/2}\) can be easily evaluated with the formula in Ref. 37, page 71. The determinant of the matrix \(N\) being \(-\sin \beta\), we find
\[
|g| = \sin^2 \beta \det(\mu^{-1}) \Lambda_A \Lambda_B \Lambda_C.
\]

The function \(\mu(\chi) = \det(\mu^{-1})\) is a complicated function of the internal rotation angles \(\chi_v\), see Eq. (A37). Due to the presence of this weight function in integrals, the operators \(p_{\chi_v}\) are non-Hermitian, even if we act only on functions satisfying the periodic boundary condition \(f(\chi_v) = f(\chi_v + 2\pi]\). It is not difficult to show that upon restriction of the operator domain to such periodic functions, we get
\[
p_{\chi_v}^+ = - \mu(\chi)^{-1/2} i \hbar \frac{\partial}{\partial \chi_v} \mu(\chi)^{1/2}.
\]
Also the operators \(j_v\) are non-Hermitian; they satisfy
\[
j_v^+ = - \Lambda_v^{-1} \mu(\chi)^{-1/2} i \hbar \frac{\partial}{\partial \chi_v} b_v(\chi_v) \mu(\chi)^{1/2},
\]
which may be compared with Eq. (A42).

Incidentally, the question may arise why \(J_v^+ = J_v\), because integration over \(\xi\) requires the weight \(\sin \beta\). This is a consequence of the relation,
\[
\sum \left[ \frac{\partial}{\partial \xi_j} (N^{-1})_{ji} \sin \beta \right] = 0.
\]
It is easy to show by means of this relation that the components of \(J\) are indeed Hermitian.
\[ 2T = \left( (\sin \beta)^{-1} p_y^T N^{-1} \sin \beta - \mu(\chi) \right)^{-1/2} p_x^T A^{-1} \]
\[ \times B^T \mu(\chi)^{1/2} \left[ N^{-1} p_z - B A^{-1} p_x \right] + \mu(\chi)^{-1/2} p_y^T A^{-1} \mu(\chi)^{1/2} p_x. \]  
(A52)

By the use of Eqs. (A49), (A50) and (A51) this may be written as
\[ T = \frac{1}{2} (J^r - j^r) \mu(j - j) + \sum \Lambda_n \mu(\chi)^{-1/2} p_x^T p_x, \]  
(A53)

with \( \Lambda_n = (I_n \chi). \) Although this operator looks similar to the classical form of Eq. (A47), its complexity is hidden in the adjoint operators defined in Eqs. (A49) and (A50). One will not explicitly need this form of the operators, however, when calculating matrix elements of the Hamiltonian. By definition, the Hermitean conjugate operators in Eqs. (A49) and (A50) act in the same way on the wave function in the bra as the original operators act on the wave function in the ket. This way of writing the kinetic energy operator in curvilinear coordinates has been discussed in general terms by Chapuisat et al.\(^\text{29}\)

**APPENDIX B: MATRIX ELEMENTS AND SELECTION RULES**

In this Appendix we will consider the selection rules of the dipole operator and matrix elements of the Coriolis coupling operator. In their evaluation use made of \( G_6 \) symmetry. Therefore, we first consider the effect of the elements of this group on the external and internal coordinates. Then we will introduce a model for the dipole and discuss its selection rules and we end by considering the matrix elements of the Coriolis operator.

From the definition of the trimer frame \( \vec{f}_r, \vec{f}_s, \) and \( \vec{f}_z, \) see Appendix A, follows immediately that \( \vec{f}_s, \) and \( \vec{f}_s, \) change sign under inversion \( E^* \) and that \( \vec{f}_z \) is invariant. So, \( E^* \) has the effect of a rotation \( R_s(\pi) \) of the frame, so that the Euler angles \( \alpha \) and \( \beta \) are invariant and \( \gamma \) is changed into \( \gamma + \pi, \) cf. Eq. (A3).

The effect of \( E^* \) on the internal coordinates follows from the fact that all position vectors in Eq. (A5) are inverted, while the frame vectors are rotated by \( R_s(\pi). \) Consequently, the internal coordinates \( d_{\alpha,i} \) transform as \( E^* d_{\alpha,i} = -R_s(\pi)d_{\alpha,i}. \) From Eq. (A30) and the observation that \( -R_s(\pi) \sigma_{xy} \) leaves \( v_x, h_x, \) and \( x_{\chi} \) invariant, since all these vectors lie in the \( xy \)-plane, it follows that \( E^* x_{\chi} = -x_{\chi}, \) for \( n = A, B, C. \)

For an equilateral triangle the frame vectors \( \vec{f}_x = N_x(2DA - DB - DC) \) and \( \vec{f}_y = N_y(DB - DC) \) are orthogonal. By inspection it follows that the permutation \((ACB) \times (153)(264)\) rotates this frame by \( R_s(-2\pi/3) \) and, thus, changes the Euler angle \( \gamma \) into \( \gamma - 2\pi/3. \) Since it also relabels the position vectors \( D^\tau_P d_{\alpha,i} \) in Eq. (A5), its effect on the internal coordinates is that \( (ACB)(153)(264)d_{\alpha,i} = R_s(2\pi/3)d_{\alpha,i}, \) etc. Substituting this into Eq. (A30) and using that \( R_s(2\pi/3)v_y = v_B, \) that \( R_s(2\pi/3)x_{\chi,i}(0) = x_{B,i}(0), \) and that \( R_s(2\pi/3)R(h_A, x_A)R_s(-2\pi/3) = R(h_B, x_A), \) we find that \((ACB)(153)(264)\chi_B = \chi_A. \) Analogously it follows that \((ACB)(153)(264)\chi_C = \chi_B \) and \((ACB)(153)(264)\chi_A = \chi_C. \) The wave functions of Eq. (9) follow now easily in the manner described in the main text.

The symmetry of the symmetric top functions \( |JKM\rangle, \) which are normalized Wigner \( D^* \) functions, follows directly from the fact that the operators \((ACB)(153)(264) \) and \( E^* \) act only on \( \chi, \) cf. The dependence of \( D^* \) on \( \gamma \) is through the factor \( \exp(i\gamma). \) When acting with the group operators on a function of the coordinates it is convenient to impose the homomorphism condition,\(^{40}\) which implies that the operators in function space are the inverse of those in coordinate space. So, in general, the symmetric top functions \( |JKM\rangle \) carry the irrep with label \( \overline{-K}. \)

In order to derive the (far-)infrared selection rules, we model the dipole function by making the assumption that this function is given by the sum of the permanent dipoles of the water monomers. Additional contributions due to polarization and other intermolecular interaction effects will not alter the symmetry of this dipole function. The permanent dipole moments are rotating with the monomers; with the use of the formulas in Appendix A it follows that the components of the dipole with respect to the trimer frame are given by

\[ \mu_{BF} = \mu_{H^2O} \sum_{n} R(h_{\nu}, x_{\nu}) R_s(\xi_{\nu} - \varphi_{\nu}) \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \]
\[ = \mu_{H^2O} \sum_{n} R_s(\xi_{\nu}) R_s(x_{\nu}) R_s(-\varphi_{\nu}) \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}. \]  
(B1)

These are the Cartesian components. If we define the spherical components

\[ \mu_{BF} = \mu_{z} \]
\[ \mu_{BF} = \frac{\mp (\mu_{z} \pm i \mu_{y})/\sqrt{2}}, \]  
(B2)

the dipole moment respect to the space-fixed frame is given by rotation with the Wigner \( D \) functions

\[ \mu_{BF} = \sum_{K} D_{mnk}^{(1)}(\alpha, \beta, \gamma) \mu_{BF}. \]  
(B3)

From the action of \((ACB)(153)(264)\) on the angles \( x_{\nu} \) and the relation \( \xi_{\nu-1} = \xi_{\nu} - 2\pi/3 \) follows that the "internal" dipole operator transforms as

\[ (ACB)(153)(264) \mu_{BF}[(ACB)(153)(264)]^{-1} \]
\[ = R_s(-2\pi/3) \mu_{BF}. \]  
(B4)

Note that, in accordance with the transformation rules of vector operators given, e.g., in Ref. 38 (page 42), this rotation is the inverse of that of the coordinate vectors. We see that \( \mu_{BF} \) is invariant under \((ACB)(153)(264)\) and that the spherical components \( \mu_{BF} \) obtain the phase factor \( \exp(\pm 2\pi/3) \). Since the action of \( E^* \) on the internal coordinates is equivalent to a reflection \( \sigma_{xy} \) respect to the

\[ \sigma_{xy}. \]
xy-plane, $E^*$ leaves $\mu_{x1}^B$ and $\mu_{x2}^B$ invariant and changes the sign of $\mu_{x3}^B$. Hence, the $\kappa = +1$ and $\kappa = -1$ components of the "internal" dipole function carry the irreps $A^+_1$ and $A^+_3$, respectively, and the $\kappa = 0$ component carries $A^-_1$. We have just seen that the "external" Wigner functions with $\kappa = 0$ transform according to the $A^-_1$ irrep and that the functions with $\kappa = +1$ and $\kappa = -1$ transform according to $A^+_3$ and $A^+_1$, respectively.

From Eq. (B3) follows now that all components of the space-fixed dipole function carry the $A^-_1$ irrep. It is obvious that this must be so, since the dipole moment is invariant under all permutations and changes sign under inversion. For the transformation properties of the internal and rotational part of the dipole function separately, we may consider also the approximate selection rules for the internal and rotational transitions separately. Parallel (c-type) transitions are associated with $\mu_{x1}^B$, perpendicular (a-type) transitions with $\mu_{x3}^B$.

We note that upon inclusion of donor tunneling and simultaneous extension of the symmetry to $G_{48}$ the dipole moment function becomes invariant under all pure permutations of this group and still changes sign under $E^*$. Dipole transitions occur only between states of the same irrep, except for the parity, which must alternate.

We now turn to the symmetry of the operators occurring in the Hamiltonian, Eq. (2). The operators $p_{x1} = -i\hbar(\partial/\partial \chi_j)$ change sign under $E^*$. The operation $(ABC)(153)(264)$ permutes their labels by the inverse of the permutation $(ABC)$ acting on the angles $\chi_j$ (because of the homomorphism condition). Since the components $j_x$ and $j_y$ of $j_z$ transform according to a reducible representation, it is more convenient to define the "shift" operators, cf. Eqs. (6) and (A44),

$$j_z = -i\hbar \sum \exp(\pm i \xi_j) \left(1 \pm i \cos \chi_j \right) \partial/\partial \chi_j.$$  \hspace{1cm} (B5)

These operators transform under the group generator $\mathcal{F}$ = $(ABC)(153)(264)$ as

$$\mathcal{F}j_z \mathcal{F}^{-1} = -\exp(\mp 2 \pi i/3)j_z = \exp(\pm \pi i/3)j_z$$  \hspace{1cm} (B6)

and, therefore, they carry the irreps $A^-_2$ and $A^+_3$ of $G_{48}$. By the irrep multiplication rule these irrep label $k$ of a function on which they act by $+1$ or $-1$. The operator $j_z$ carries the totally symmetric irrep $A^-_3$. The components of the body-fixed form of the angular momentum $J_+$ and $J_-$ transform according to the $A^-_3$ and $A^+_3$ irreps, respectively, while $J_z$ carries the $A^+_1$ irrep.

The matrix elements of $j_z$ and $j_\mu$ over the functions $\Phi_k$ can be considerably simplified by the use of the $G_6$ symmetry. The operator $j_\mu$, carrying the $A^+_1$ irrep, yields only diagonal elements.

$$\langle \Phi_k | j_\mu | \Phi_k \rangle = \sum_{n=\pm 1} \exp(-nk\pi i/3)\langle uud|j_\mu|\mathcal{F}^nuud \rangle.$$  \hspace{1cm} (B7)

Because of the factor $-i\hbar$ in $j_\mu$, see Eq. (A44), the terms with $n = 0$ and $n = 3$ are pure imaginary. Since $\langle uud|j_\mu|\mathcal{F}^nuud \rangle = \langle uud|j_\mu|\mathcal{F}^{-n}uud \rangle$ the sums of the terms with $n = \pm 1$ and $n = \pm 2$ are pure imaginary too. Hence, the expectation values of $j_\mu$ are pure imaginary. The expectation value of $j_\mu$ is the complex conjugate of the expectation value of $j_z$ and, therefore, exactly the opposite of the latter. And, since it is the sum operator $j_\mu = j_z^2$ which occurs in $H^{Cor}$, we do not find any first order Coriolis coupling with the overall angular momentum $\langle JKM | \mathcal{F}^n JKM \rangle = K$.

The only non-vanishing matrix elements of $j_\mu$ are

$$\langle \Phi_k \pm 1 | j_\mu | \Phi_k \rangle = \sum_{n=\pm 1} \exp(-nk\pi i/3) \mathcal{F}^nuud|j_\mu|uud \rangle.$$  \hspace{1cm} (B8)

and

$$\langle \Phi_k | j_\mu | \Phi_k \rangle = \langle \Phi_k | j_\mu | \Phi_{k+1} \rangle^* = \sum_{n=\pm 1} \exp(-nk\pi i/3) \langle \mathcal{F}^nuud|j_\mu|uud \rangle^*.$$  \hspace{1cm} (B9)

The functions $u$ and $d$ are real and the shift operators, given by Eq. (B5), behave under complex conjugation as $(j_z)^* = -j_z$. Since the matrix elements of $j_\mu$ in Eqs. (B8) and (B9) get opposite signs then, it is immediately obvious that the terms with $n = 0$ cancel when we take the combination $j_z^2 = j_\mu$ in which these operators appear in $H^{Cor}$. The remaining terms can be reduced to one-particle integrals. Given that $\xi_\nu = \xi_\lambda + (\nu - 1)2\pi/3$, we may rewrite Eq. (B5) as in Eqs. (22) and (23) of the main text. The one-particle operators $l_\pm$ [Eq. (22)] change sign under inversion, $E^*\chi = -\chi$, the one-particle functions are related as $\langle d(\chi) = u(-\chi)$, and the matrix elements obey

$$\langle u|l_\pm|d \rangle = -\langle d|l_\pm|u \rangle$$  \hspace{1cm} (B10)

Note further that the one-particle operators $l_\pm$ behave under complex conjugation as $(l_\pm)^* = -l_\pm$. For the single-flip terms with $n = \pm 1$ we obtain

$$\langle \Phi_k \pm 1 | j_\mu + j_\mu^* | \Phi_k \rangle = \exp(-k\pi i/3)(\langle uud|j_\mu|uud \rangle - \langle udd|j_\mu|uud \rangle)$$

and

$$+ \exp(k\pi i/3)(\langle uud|j_\mu|uud \rangle - \langle udd|j_\mu|uud \rangle).$$

$$= 4\exp(\pm 2\pi i/3)\cos(k\pi/3)\langle |u|l_\pm|d \rangle.$$  \hspace{1cm} (B11)

All other terms in this expression, which are proportional to the overlap integral $S = \langle u|d \rangle$, have canceled. The terms with $n = \pm 2$ and $n = 3$ represent multiple flips and are of higher order in the (differential) overlap between $u$ and $d$. Also the
normalization of $\Phi_\pm$ and $\Phi_{\pm 1}$ leads to terms of higher order, which are expected to be relatively small. Summarizing, we find that a good estimate of the size and $k$-dependence of the only non-vanishing shift matrix elements can be obtained from Eq. (B11).

### APPENDIX C: $G_{48}$ SYMMETRY ADAPTATION

Starting from the functions $\Phi_\pm$ in Eq. (9) adapted to $G_6$, we will describe in this Appendix how to obtain functions adapted to $G_{48}$. We immediately qualify this statement by noting that both $G_{48}$ and $G_6$ are direct products, $G_{48}=G_{24}\otimes\{E,E^*\}$ and $G_6=C_3\otimes\{E,E^*\}$. Since parity adaptation only requires acting with $E\pm E^*$, we will concentrate in this Appendix on the groups $G_{24}$ and $C_3$, rather than on $G_{48}$ and $G_6$. Accordingly, we write the $G_6$ irrep label as $k = (j, \pm)$ with $j = 0, 1, -1$ and $\Phi_\pm = \frac{1}{2}(E \pm E^*) \Phi_j$, where $j$ labels the $C_3$ irrep. Note that $j$ does not run from 1 to 3, as in the main text, and that until further notice we omit the parity label $\pm$. Below we will employ idempotent operators generating functions that are not necessarily normalized to unity. So, take also note that the normalization of functions in this Appendix differs somewhat from the normalization used in the main text.

Let us consider first the decomposition of the eight-dimensional induced representation $j|G_{24}$, spanned by $\{C\Phi_j\}$, where the elements $C$ are coset generators of $C_3 \subset G_{24}$. By the Frobenius reciprocity theorem, an irrep $\Gamma$ of $G_{48}$ occurs in $j|G_{24}$ with the same multiplicity as the irrep $j$ in $\Gamma$. From Table I we get

\begin{align}
j = 0 \quad (\equiv A_1) | G_{24} &= A_1 \oplus A_1 \oplus T_6 \oplus T_3, \\
j = 1 \quad (\equiv A_2) | G_{24} &= A_2 \oplus A_2 \oplus T_6 \oplus T_3, \\
j = -1 \quad (\equiv A_3) | G_{24} &= A_3 \oplus A_3 \oplus T_6 \oplus T_3.
\end{align}

In order to explicitly adapt $\Phi_j$ to $G_{24}$, it is convenient to go along the group chain $C_3 \subset G_{12} \subset G_{24}$, where the intermediate group $G_{12}$ arises since also $G_{12}$ is a direct product: $G_{24} = \{E,(12)(34)(56)\} \rtimes G_{12}$. The second step, i.e., the adaptation of a $G_{12}$ adapted function to $G_{24}$, is easy in view of the direct product structure of $G_{24}$; it simply requires the action of $E \pm (12)(34)(56)$. The $C_3 \subset G_{12}$ step is more complicated. Here it is useful to choose the $T$ irrep of $G_{12}$ such that upon restriction of this irrep to $C_3$ the matrices representing $C_3$ are diagonal. This process is sometimes called "sequence-adapting" the irrep. (The one-dimensional irreps are of course automatically sequence-adapted.)

Given the matrices of the irrep $T$ of the point group $T$, tabulated in Ref. 42, p. 291, we have deduced the similarity transformation that diagonalizes the matrices of $C_3$. The corresponding matrices that represent the coset generators of $C_3 \subset G_{12}$ in this sequence-adapted irrep are

\begin{align}
D^T[\{(12)(34)\}] &= \frac{1}{3} \begin{pmatrix} -1 & 2 & 2 \\ 2 & -1 & 2 \\ 2 & 2 & -1 \end{pmatrix}, \\
D^T[\{(12)(56)\}] &= \frac{1}{3} \begin{pmatrix} -1 & 2 & 2^* \\ 2^* & -1 & 2 \\ 2 & 2^* & -1 \end{pmatrix}, \\
D^T[\{(34)(56)\}] &= \frac{1}{3} \begin{pmatrix} -1 & 2 & 2^* \\ 2^* & -1 & 2 \\ 2 & 2^* & -1 \end{pmatrix}.
\end{align}

with $\epsilon = \exp(2\pi i/3)$. Upon restriction to $C_3$ this irrep becomes $A_1 \oplus A_2 \oplus A_3$. The step to $G_{24}$ is made by realizing that $(12)(34)(56)$ is represented by the unit matrix for the $g$ irreps and by minus the unit matrix for the $u$ irreps. Further we notice the multiplication rules, such as $(12)(34) \times (12)(34)(56) = (56)$, etc.

We next define the well-known elements $41$ carrying the irreducible subspaces of the group algebra of a group $G$ of order $|G|

\begin{align}
W^{T}_{ij} &= \frac{f^T}{|G|} \sum_{g \in G} D^T(g^{-1})_{ij}g.
\end{align}

These operators have the following properties:

\begin{align}
g W^{T}_{ij} &= \sum_{k=1}^{f^T} W^{T}_{kj} D^T(g)_{ki}, \quad g \in G, \\
(W^{T}_{ij})_{k} &= W^{T}_{kj}, \\
W^{T}_{ij}, W^{T}_{ji} &= \delta_{\Gamma^\prime \Gamma} \delta_{i^\prime i} W^{T}_{j^\prime j}.
\end{align}

Equation (C4a) shows that the action of $W^{T}_{ij}$ onto a wave function yields a result that either transforms according to $\Gamma$ or the function vanishes.

In order to predict whether we obtain a vanishing result, we define the orthogonal $C_3$ projectors $O_j$ ($j = 0, 1, -1$) and the "reduced" operator belonging to the irrep $\Gamma$ of $G_{12}$

\begin{align}
\bar{W}^{T}_{ij} &= \frac{f^T}{4} \sum_C D^T(C^{-1})_{ij}C.
\end{align}

where $C$ runs now only over the coset generators of $C_3 \subset G_{12}$. Observe that if $\Gamma$ is one-dimensional, the matrix elements $D^T(C^{-1})_{ij}$ are simply characters of $C$.

The sequence adaptation of the $G_{12}$ irrep $T$ to $C_3$ implies that the rows and columns of this irrep are labeled by $j = 0, 1, -1$, which in turn yields the equation

\begin{align}
W^{T}_{ji} = \bar{W}^{T}_{ji}, O_j.
\end{align}

Since $\Phi_j = O_j \Phi_j$ and $O_j O_{j^*} = \delta_{j^* j} O_j$ it follows that $W^{T}_{ji}, \Phi_{j^*} \neq 0$ if and only if $j^* = j$. If $\Gamma$ is one-dimensional then only a nonvanishing result is obtained if $j$ is contained in the induced representation, cf. Eq. (C1).
Multiplication of the $G_{12}$ operator $W_{ij}^1$ by $\frac{1}{2} (E \pm (12) \times (34)(56))$ gives the corresponding $G_{24}$ operator, which we will also label with $\Gamma$. Assuming now that we have chosen $j$ and $k=(j, \pm)$ such that that $|\Psi_{ij}^\pm| = \frac{1}{2} O_j(E \pm E^*)|uud\rangle$, we find from the idempotence of $O_j$ that $W_{ij}^1|\Phi_k\rangle = \frac{1}{2} W_{ij}^1(E \pm E^*)|uud\rangle$. Thus by Eqs. (C4b) and (C4c), the commutation of $H_{un}$ with $G_{12}$, and the turn-over rule for we obtain

$$
\langle \Psi_{ij}^\pm | H_{un} | \Psi_{ij}^\pm \rangle = \frac{1}{2} \delta_{ij} (uud)|H_{un}|W_{ij}^1 \times (E \pm E^*)|uud\rangle,
$$

(C7)

and after substitution of Eqs. (C6) and (C5) we obtain the equation used to arrive at Eq. (16) of the main text. Functions belonging to different irreps of $G_{48}$ are non-interacting under $H_{un}$, of course.

---