# Pseudorotation tunneling in several water trimer isotopomers 

M. Geleijns and A. van der Avoird<br>Institute of Theoretical Chemistry, NSR-Center, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

(Received 19 June 1998; accepted 29 September 1998)


#### Abstract

The tunneling dynamics of several water trimer isotopomers is investigated by using an extension of the Hamiltonian that was previously derived for pure (more symmetric) trimers. This Hamiltonian takes into account the overall rotation of the trimer and three internal, torsional, or pseudorotational, motions of the monomers. Quantitative calculations of the torsional levels are presented, and the small effects of internal, i.e., hydrogen bonded, H/D substitutions and the much larger effects of external H/D substitutions are discussed. Transition line strengths are computed as well, and the assignment of most of the bands observed for the various water trimer isotopomers is confirmed. In one case we suggest a different assignment. © 1999 American Institute of Physics. [S0021-9606(99)03501-1]


## I. INTRODUCTION

Because of the importance of water in many facets of our lives and the desire to better understand the properties of this solvent, water clusters are under active investigation. The water dimer has been studied extensively over a number of years, ${ }^{1-3}$ while considerable progress is now also being made for the trimer and larger clusters. ${ }^{4-49}$ In this article we concentrate on the water trimer; information on the structure of this hydrogen bonded complex and its tunneling dynamics is available from high-resolution far-infrared spectra ${ }^{8,18-20,43}$ and from theoretical studies of the vibration-rotationtunneling (VRT) states. ${ }^{11,12,25,26,28,29,31,32}$ The spectra reveal that the isotopically pure species, $\left(\mathrm{H}_{2} \mathrm{O}\right)_{3}$ and $\left(\mathrm{D}_{2} \mathrm{O}\right)_{3}$, are oblate symmetric rotors, due to the dynamical averaging over six asymmetric global minimum structures which were predicted by ab initio calculations. ${ }^{4,7,11-17,21,24-27,30,35,36,41}$ This averaging is the result of a low barrier motion in which the external protons (or deuterons) of the cluster flip through the plane of the hydrogen-bonded triangular "skeleton." This flipping motion is sometimes called pseudorotation, ${ }^{11,18,28,29}$ because the tunneling process is equivalent to a rotation of $120^{\circ}$ around the $C_{3}$ axis. In two previous articles ${ }^{31,32}$ we derived and applied a Hamiltonian for this tunneling motion, which takes into account the three internal torsional coordinates that correspond to the pseudorotation tunneling, the overall rotation of the trimer, and the (Coriolis) coupling between these two.

Recently, attention has also been drawn to the mixed isotopomers. In 1996, Sabo et al. ${ }^{50}$ presented a threedimensional model calculation of the low-frequency intermolecular torsional levels of the $\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\left(\mathrm{D}_{2} \mathrm{O}\right)$ and $\left(\mathrm{D}_{2} \mathrm{O}\right)_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)$ trimers. Sorenson et al. ${ }^{51}$ made a diffusion Monte Carlo study of several isotopomers, but they were only able to estimate the tunneling splitting of symmetric systems, thus being restricted to (HDO) $)_{3}$. Experimental data are still not available for the above-mentioned isotopomers, but, in the same year, a band was found for the $\left(\mathrm{D}_{2} \mathrm{O}\right)_{2}(\mathrm{HDO})$ trimer with the H atom external, i.e., nonhy-
drogen bonded. ${ }^{52}$ In recent high-resolution far-infrared spectroscopy experiments of Viant et al., ${ }^{53}$ detailed information has been obtained on the VRT dynamics of this and five other mixed isotopomers. For each isotopomer (see Fig. 1) a single $c$-type (parallel) VRT band was observed (see Table I). With regard to the nomenclature of the different isotopomers, we adopt the labeling of Viant et al..${ }^{53}$ a species with $n$ deuterons is denoted $d_{n}$, together with the letter " $a$ ', or ' $b$ '" if there are two isotopomers investigated with the same number of deuterons. For instance, (HDO) $)_{3}$ is named $d_{3} a$, because two isotopomers with this number of deuterons were measured, and a distinction is made between $d_{3} a$, with all protons hydrogen bonded, and $d_{3} b$, where one of the protons is external. An exception is, of course, $\left(\mathrm{H}_{2} \mathrm{O}\right)_{3}$, which has no deuterons; it is labeled $h_{6}$.

In this article, the model that we previously used ${ }^{31,32}$ to describe the tunneling motions in the pure species, $\left(\mathrm{H}_{2} \mathrm{O}\right)_{3}$ and $\left(\mathrm{D}_{2} \mathrm{O}\right)_{3}$, is extended to other isotopomers. In this model we made use of the permutation-inversion symmetry: the torsional levels belong to the irreducible representations of the group $G_{6}$ or $\operatorname{PI}\left(C_{3 h}\right)$. In the mixed trimers, with the exception of $(\mathrm{HDO})_{3}$, the symmetry of the internal motions is broken and, simultaneously, the degeneracy of the oblate symmetric rotor levels is lifted by asymmetry doubling. Calculations were performed for the six isotopomers measured by Viant et al., with the use of the extended model. The results are compared with the experimental data.

## II. THEORY

Our model Hamiltonian for the water trimer is introduced in this section. The kinetic energy operator describes the overall rotation and the rotation of the three external protons/deuterons around the axes connecting the monomer centers of mass and the hydrogen bonded protons/deuterons. The latter motion, which involves the tunneling of the external protons through the plane of the trimer, is referred to as pseudorotation tunneling or torsion. The monomers them-







FIG. 1. Nomenclature of the mixed isotopomers.
selves are kept rigid, while in our restricted-dimensionality model their centers of mass constitute a rigid triangle formed by hydrogen bonds (see Fig. 2). The monomer rotations are described by three rotation angles $\chi_{\nu}$, where $\nu=A, B, C$ labels the monomers. The overall rotation is described by the three Euler angles $(\alpha, \beta, \gamma)$. In our previous article ${ }^{31}$ the following kinetic energy operator was derived

$$
\begin{equation*}
T=\frac{1}{2}\left(\boldsymbol{J}-\boldsymbol{j}^{\dagger}\right) \boldsymbol{\mu}(\boldsymbol{\chi})(\boldsymbol{J}-\boldsymbol{j})+\frac{1}{2} \sum_{\nu} \Lambda_{\nu}^{-1} p_{\chi_{\nu}}^{\dagger} p_{\chi_{\nu}} \tag{1}
\end{equation*}
$$

where $\boldsymbol{J}$ and $\boldsymbol{j}=\Sigma_{{ }_{j}} \boldsymbol{j}_{\nu}$ are the total angular momentum operators for the trimer and the monomers, respectively, $\boldsymbol{\mu}(\boldsymbol{\chi})$ is the inverse inertia tensor of the trimer, and $\Lambda_{\nu}$ is the effec-

TABLE I. Observed transitions for the eight isotopomers. The nomenclature corresponds with Fig. 1. Frequencies are in $\mathrm{cm}^{-1}$.

|  | Experiment |  |  |
| :---: | :---: | :---: | :---: |
|  | Frequency $^{\mathrm{b}}$ | Type $^{\mathrm{c}}$ | Assignment <br>  <br>  <br>  <br>  <br> $h_{6}$ |
|  | 65.6 | $\perp$ | $4, i$ |
| $d_{3} a$ | 87.1 | $\\|$ | $6 \leftarrow 1$ |
| $d_{3} b$ | 45.8 | $\\|$ | $6 \leftarrow 1$ |
| $d_{4} a$ | 45.9 | $\\|$ | $5 \leftarrow 2$ |
| $d_{4} b$ | 44.4 | $\\|$ | $6 \leftarrow 1$ |
| $d_{5} a$ | 46.5 | $\\|$ | $5 \leftarrow 2$ |
| $d_{5} b$ | 42.8 | $\\|$ | $6 \leftarrow 1$ |
| $d_{6}$ | 97.3 | $\\|$ | $7 \leftarrow 1$ |
|  | 27.5 | $\perp$ | $4,5 \leftarrow 1$ |
|  | 41.1 | $\\|$ | $6 \leftarrow 1$ |
|  | 82.5 | $\perp$ | $7 \leftarrow 2,3$ |
|  | 89.6 | $\\|$ | $8,9 \leftarrow 2,3$ |
|  | 98.1 | $\perp$ | $8,9 \leftarrow 1$ |

${ }^{\text {a}}$ From Refs. 28,43,52,53.
${ }^{\mathrm{b}}$ From Refs. 8,18-20,43,52,53,59.
${ }^{\text {c }}$ Parallel ( $c$-type) or perpendicular ( $a$-type) transition.


FIG. 2. Planar reference geometry of the water trimer $\left(\chi_{A}=\chi_{B}=\chi_{C}=0\right)$.
tive moment of inertia of monomer $\nu$ about its fixed axis of rotation. The operators $\boldsymbol{j}_{\nu}$ associated with the rotations of the monomers $\nu=A, B, C$ about fixed axes are not standard angular momentum operators. Explicit expressions for their components in terms of the torsional angles $\chi_{\nu}$ are given in Eqs. (A44) and (B5) of Ref. 31. These operators are nonHermitian. Even the operators $p_{\chi_{\nu}}=-i \hbar \partial / \partial \chi_{\nu}$ are nonHermitian if one takes into account that the weight associated with the internal coordinates $\boldsymbol{\chi}$ and the Euler angles $(\alpha, \beta, \gamma)$ is $\operatorname{det}[\boldsymbol{\mu}(\boldsymbol{\chi})]^{-1 / 2} \sin \beta\left(\Lambda_{A} \Lambda_{B} \Lambda_{C}\right)^{1 / 2}$, which is a function of the $\chi_{\nu}$. Therefore, Eq. (1) must explicitly contain the Hermitian conjugate operators $\boldsymbol{j}^{\dagger}$ and $p_{\chi_{\nu}}^{\dagger}$.

The formula in Eq. (1) holds for all isotopomers. The (inverse of the) $\boldsymbol{\mu}$ tensor in principle is a function of $\boldsymbol{\chi}$, but the $\boldsymbol{\chi}$-dependent terms only contribute about $1 \%$ of the inertia tensor and may be neglected. ${ }^{31}$ Then, the inertia tensor $\boldsymbol{\mu}^{-1}$ is constant; it is simply determined by the monomer masses, considered as point masses, placed at the vertices of a (rigid) triangle. The operator $p_{\chi_{\nu}}$ becomes Hermitian, but $\boldsymbol{j}$ does not. In general, one should diagonalize the inverse inertia tensor $\boldsymbol{\mu}$ to obtain the rotational constants, but as we consider only trimers with at least two monomers identical, $\boldsymbol{\mu}$ is automatically diagonal in the coordinate system of Fig. 2. That is, the $z$ axis normal to the triangle is always a principal axis, and if we place the 'unique" monomer with its mass center on the $x$ axis, the $x$ and $y$ axes in Fig. 2 are principal axes as well. The trimer rotational constants are defined as: $A=\frac{1}{2} \mu_{x x}, B=\frac{1}{2} \mu_{y y}$, and $C=\frac{1}{2} \mu_{z z}$ if the "unique" monomer has a mass larger than the other two monomers. If its mass is smaller, then $B=\frac{1}{2} \mu_{x x}$ and $A$ $=\frac{1}{2} \mu_{y y}$. For the symmetric rotor case $A=B$.

The Hamiltonian in Eq. (1) can be partitioned into an overall rotational part $H^{\text {rot }}$, an internal part for the monomer motions, $H^{\text {int }}$, and a coupling term $H^{\text {Cor }}$, the Coriolis coupling. The overall rotation term is

$$
\begin{align*}
H^{\mathrm{rot}}= & A J_{x}^{2}+B J_{y}^{2}+C J_{z}^{2} \\
= & \frac{1}{4}(A+B)\left(J_{-} J_{+}+J_{+} J_{-}\right) \\
& +\frac{1}{4}(A-B)\left(J_{-}^{2}-J_{+}^{2}\right)+C J_{z}^{2} . \tag{2}
\end{align*}
$$

The torsional motions of the monomers are described by

$$
\begin{align*}
H^{\mathrm{int}}= & \sum_{\nu} \frac{-\hbar^{2}}{2 \Lambda_{\nu}} \frac{\partial^{2}}{\partial \chi_{\nu}^{2}}+\frac{1}{4}(A+B)\left(j_{+}^{\dagger} j_{+}+j_{-}^{\dagger} j_{-}\right) \\
& +\frac{1}{4}(A-B)\left(j_{+}^{\dagger} j_{-}+j_{-}^{\dagger} j_{+}\right)+C j_{z}^{\dagger} j_{z} \\
& +V\left(\chi_{A}, \chi_{B}, \chi_{C}\right) \tag{3}
\end{align*}
$$

in which the last term is the potential, a function of the three torsional angles $\chi_{\nu}$. All terms linear in both $\boldsymbol{J}$ and $\boldsymbol{j}$ form the Coriolis part of the Hamiltonian that couples the overall rotation with the torsional motions

$$
\begin{align*}
H^{\mathrm{Cor}}= & -\frac{1}{4}(A+B)\left[\left(j_{+}+j_{-}^{\dagger}\right) J_{+}+\left(j_{-}+j_{+}^{\dagger}\right) J_{-}\right] \\
& -\frac{1}{4}(A-B)\left[\left(j_{-}+j_{+}^{\dagger}\right) J_{+}+\left(j_{+}+j_{-}^{\dagger}\right) J_{-}\right] \\
& -C\left(j_{z}+j_{z}^{\dagger}\right) J_{z} . \tag{4}
\end{align*}
$$

Note that the terms with ( $A-B$ ) in Eqs.(2), (3), and (4) did not occur in the Hamiltonian which we used in Ref. 31; they are due to the lower symmetry of mixed isotopomers.

The pseudorotation tunneling levels are the eigenvalues of the complete Hamiltonian. The observed bands in the farinfrared spectra ${ }^{52,53}$ correspond to transitions between these levels. In order to facilitate the assignment of these measured bands, it is useful to know the line strengths of the transitions as well. The dipole function with respect to the trimer frame is given in Eq. (B1) of Ref. 31

$$
\begin{equation*}
\boldsymbol{\mu}^{\mathrm{BF}}(\boldsymbol{\chi})=\sum_{\nu} \boldsymbol{R}_{z}\left(\xi_{\nu}\right) \boldsymbol{R}_{x}\left(\chi_{\nu}\right) \boldsymbol{R}_{z}\left(-\eta_{\nu}\right) \boldsymbol{\mu}_{\nu} \tag{5}
\end{equation*}
$$

The vector $\boldsymbol{\mu}_{\nu}$ is the dipole moment vector of a molecule $\mathrm{H}_{2} \mathrm{O} / \mathrm{D}_{2} \mathrm{O} / \mathrm{HDO}$, expressed with respect to the principal axes frame of this molecule $\nu$. It is assumed here that the dipole of the trimer is simply the sum of the permanent dipoles of the monomers. Equation (5) describes the rotation of the monomer dipole moments to the trimer frame in Fig. 2. This transformation involves the fixed angles $\eta_{\nu}$ (the angle between the dipole of monomer $\nu$ and its axis of rotation) and $\xi_{\nu}$ (which defines the axis of rotation with respect to the trimer frame), as well as the dynamical variables $\chi_{\nu}$, the torsional angles. The rotation matrices $\boldsymbol{R}$ are given, in the active rotation convention, by

$$
\boldsymbol{R}_{z}(\alpha)=\left(\begin{array}{ccc}
\cos \alpha & -\sin \alpha & 0  \tag{6}\\
\sin \alpha & \cos \alpha & 0 \\
0 & 0 & 1
\end{array}\right)
$$

and

$$
\boldsymbol{R}_{x}(\alpha)=\left(\begin{array}{ccc}
1 & 0 & 0 \\
0 & \cos \alpha & -\sin \alpha \\
0 & \sin \alpha & \cos \alpha
\end{array}\right)
$$

Note that for $\mathrm{H}_{2} \mathrm{O}$ and $\mathrm{D}_{2} \mathrm{O}$, where the dipole lies along the $C_{2}$ axis (which is assumed to be the monomer $x$ axis), the angle $\eta_{\nu}$ is the same as the angle $\varphi_{\nu}$ in Fig. 2, whereas for HDO the dipole vector does not coincide with one of the principal axes.

Given the dipole operator, the line strength of the transition from level $i$ to level $f$ is

$$
\begin{equation*}
\left.S(f \leftarrow i)=\sum_{m=x, y, z}\left|\left\langle\psi_{f}\right| \mu_{m}^{\mathrm{BF}}\right| \psi_{i}\right\rangle\left.\right|^{2}, \tag{7}
\end{equation*}
$$

which can be decomposed into a parallel $(z)$ and a perpendicular $(x, y)$ part. In case of degenerate levels the line strength is obtained by summing over final states and averaging over initial states. Here we compute only the vibrational transition line strengths; for individual rovibrational transitions these must be multiplied by the Hönl-London factors. ${ }^{54,55}$

## III. COMPUTATIONAL METHOD

The pseudorotation tunneling manifold for $J=0$ was obtained by diagonalizing $H^{\text {int }}$ in a discrete variable representation (DVR) consisting of products $\xi_{n_{A}}\left(\chi_{A}\right) \xi_{n_{B}}\left(\chi_{B}\right) \xi_{n_{C}}\left(\chi_{C}\right)$ of three sinc functions ${ }^{56,57}$

$$
\begin{equation*}
\xi_{n}(\chi)=\Delta^{-1 / 2} \operatorname{sinc}\left[\pi\left(\frac{\chi}{\Delta}-n\right)\right] \tag{8}
\end{equation*}
$$

where $\Delta$ is the spacing of the DVR grid. Reference 32 contains the explicit expressions for the matrix elements of the Hamiltonian in the DVR basis. We do not need the explicit form—given in Eq. (A50) of Ref. 31—of the conjugate operators $\boldsymbol{j}^{\dagger}$, since one can apply the turnover rule to replace matrix elements of the Hermitian conjugate operators by the corresponding expressions with the original operators. The only term which did not occur in Ref. 32 contains the operator $j_{+}^{\dagger} j_{-}+j_{-}^{\dagger} j_{+}$, which gives rise to operators of the form

$$
\begin{align*}
\frac{\partial}{\partial \chi} & \cos \chi \frac{\partial}{\partial \chi} \\
& =\frac{1}{2}\left\{\cos \chi \frac{\partial^{2}}{\partial \chi^{2}}+\frac{\partial^{2}}{\partial \chi^{2}} \cos \chi-\left[\sin \chi, \frac{\partial}{\partial \chi}\right]\right\} \tag{9}
\end{align*}
$$

TABLE II. Rotational constants of the different trimer isotopomers and the effective monomer rotational constants (in $\mathrm{cm}^{-1}$ ).

|  | $h_{6}$ | $d_{3} a$ | $d_{3} b$ | $d_{4} a$ | $d_{4} b$ | $d_{5} a$ | $d_{5} b$ | $d_{6}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $A$ | 0.22172 | 0.19817 | 0.21611 | 0.19866 | 0.21436 | 0.19707 | 0.20667 | 0.19334 |
| $B$ | $=A$ | $=A$ | 0.20347 | 0.19454 | 0.20172 | 0.19290 | 0.19460 | $=A$ |
| $C$ | 0.11257 | 0.09908 | 0.10480 | 0.09829 | 0.10392 | 0.09748 | 0.10023 | 0.10302 |
|  |  | $\mathrm{H}_{2} \mathrm{O}$ | HDO (deuteron bound) | HDO (proton bound) | $\mathrm{D}_{2} \mathrm{O}$ |  |  |  |
| $\frac{\hbar^{2}}{2 \Lambda}$ | 21.3910058 | 21.3910057 | 11.7249276 | 11.7249277 |  |  |  |  |

The form on the left-hand side is rewritten, while keeping it Hermitian, in order to take advantage of the fact that local (multiplicative) operators are diagonal in the DVR.

A grid spacing of $16^{\circ}$ was used in our calculations and the grid was limited to $-112^{\circ} \leqslant \chi_{\nu} \leqslant+112^{\circ}$, since the potential becomes very high beyond this range. Note, moreover, that one of the potentials (see below) is expanded in polynomials of $\chi_{\nu}$ and starts to behave anomalously for $\chi$ values outside this range. In calculations for $J>0$ the DVR basis was multiplied by symmetric rotor functions $|J K M\rangle$ $=\left[(2 J+1) / 8 \pi^{2}\right]^{1 / 2} D_{M K}^{(J)}(\alpha, \beta, \gamma)^{*}$ for the overall rotations, with the exact quantum numbers $J$ and $M$ fixed, and $K$ $=-J,-J+1, \ldots, J$. The (ground state) values of the rotational constants $A$ and $B$ of all the trimers considered and the constants $C$ of $\left(\mathrm{D}_{2} \mathrm{O}\right)_{3}$ and $\left(\mathrm{H}_{2} \mathrm{O}\right)_{3}$ were taken from experiment. ${ }^{18,43}$ For the mixed isotopomers, where only parallel bands were observed and the values of $C$ could not be determined experimentally, it was assumed that $C^{-1}=A^{-1}$ $+B^{-1}$. This relation follows from the (quasi-)planar structure of the water trimer. The monomer moments of inertia $\Lambda_{\nu}$ were obtained from Eq. (3) of Ref. 31. All monomer $\mathrm{O}-\mathrm{H}$ bond lengths were fixed at $0.9572 \AA$, also those of the $\mathrm{O}-\mathrm{H}$ groups involved in hydrogen bonding, and all mono-
mer bond angles at $104.5^{\circ}$. The angle between the monomer rotation axes and the axes connecting the centers of mass of the monomers was kept fixed at $20^{\circ}$ for all isotopomers. ${ }^{22,23,28}$ The trimer rotational constants and the effective monomer rotational constants $\hbar^{2} /\left(2 \Lambda_{\nu}\right)$ are listed in Table II.

Two different water trimer potentials were used in the calculations. The first one is the potential of the Van Duijneveldts-referred to as the DD potential ${ }^{23,58}$ —which was obtained by fitting an eighth-degree polynomial expansion to $a b$ initio calculated interaction energies. This expansion is only valid in the range $-112^{\circ} \leqslant \chi_{\nu} \leqslant+112^{\circ}$. Second, we applied the potential of Bürgi et al., the BGLK potential. ${ }^{22}$ This modEPEN potential is an analytic site-site potential with parameters fitted to $a b$ initio calculations. Both potentials are functions of the three torsional angles only.

## IV. RESULTS AND DISCUSSION

The pseudorotation tunneling levels for $J=0$ for the different isotopomers-including the pure species-are given in Table III (DD potential) and Table IV (BGLK potential). Table V lists the line strengths of the transitions between the lower levels, separated into their parallel ( $c$-type) and per

TABLE III. Water trimer flipping frequencies (in $\mathrm{cm}^{-1}$ ), calculated with the DD potential.

| Level | $h_{6}$ | $d_{3} a$ | $d_{3} b$ | $d_{4} a$ | $d_{4} b$ | $d_{5} a$ | $d_{5} b$ | $d_{6}$ |
| :---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: |
| zero point <br> energy | 250.72 | 201.41 | 233.68 | 201.40 | 233.67 | 201.39 | 216.55 | 201.38 |
| 1 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 2 | 19.91 | 7.68 | 7.24 | 7.68 | 7.23 | 7.67 | 4.40 | 7.68 |
| 3 | 19.91 | 7.68 | 24.84 | 7.69 | 24.83 | 7.69 | 20.60 | 7.68 |
| 4 | 59.01 | 25.20 | 41.69 | 25.19 | 41.68 | 25.18 | 32.18 | 25.18 |
| 5 | 59.01 | 25.20 | 54.73 | 25.19 | 54.72 | 25.19 | 44.04 | 25.18 |
| 6 | 81.19 | 36.64 | 67.83 | 36.63 | 67.82 | 36.62 | 53.75 | 36.61 |
| 7 | 160.83 | 96.19 | 123.83 | 96.18 | 123.82 | 96.16 | 110.36 | 96.14 |
| 8 | 165.11 | 107.54 | 127.49 | 107.52 | 127.48 | 107.50 | 116.15 | 107.50 |
| 9 | 171.91 | 107.54 | 158.16 | 107.54 | 158.15 | 107.52 | 124.75 | 107.50 |
| 10 | 171.91 | 129.78 | 162.87 | 129.76 | 162.86 | 129.75 | 137.42 | 129.74 |
| 11 | 175.77 | 129.78 | 165.97 | 129.78 | 165.95 | 129.77 | 155.92 | 129.74 |
| 12 | 209.00 | 132.50 | 179.51 | 132.49 | 179.49 | 132.48 | 156.93 | 132.47 |
| 13 | 209.00 | 143.23 | 185.41 | 143.22 | 185.39 | 143.22 | 169.13 | 143.22 |
| 14 | 229.04 | 155.04 | 196.70 | 155.04 | 196.69 | 155.03 | 175.17 | 155.03 |
| 15 | 237.62 | 165.36 | 197.48 | 165.32 | 197.46 | 165.31 | 177.97 | 165.31 |
| 16 | 237.62 | 165.36 | 212.18 | 165.36 | 212.17 | 165.34 | 187.57 | 165.31 |
| 17 | 248.17 | 166.94 | 213.17 | 166.91 | 213.15 | 166.89 | 197.19 | 166.89 |
| 18 | 248.17 | 166.94 | 233.79 | 166.93 | 233.78 | 166.92 | 200.09 | 166.89 |
| 19 | 288.07 | 191.49 | 235.52 | 191.46 | 235.51 | 191.44 | 209.23 | 191.41 |

TABLE IV. Water trimer flipping frequencies (in $\mathrm{cm}^{-1}$ ), calculated with the BGLK potential.

| Level | $h_{6}$ | $d_{3} a$ | $d_{3} b$ | $d_{4} a$ | $d_{4} b$ | $d_{5} a$ | $d_{5} b$ | $d_{6}$ |
| :---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: |
| zero point <br> energy | 281.71 | 224.95 | 261.34 | 224.94 | 261.33 | 224.93 | 241.27 | 224.92 |
| 1 |  |  |  |  |  |  |  |  |
| 2 | 13.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 3 | 13.97 | 5.15 | 3.83 | 5.14 | 3.83 | 5.14 | 1.97 | 5.15 |
| 4 | 44.14 | 17.17 | 20.57 | 51.53 | 17.15 | 20.57 | 5.15 | 18.72 |
| 5 | 44.14 | 17.17 | 42.85 | 17.17 | 31.52 | 17.16 | 26.06 | 17.15 |
| 6 | 62.32 | 24.75 | 51.70 | 24.75 | 51.69 | 17.16 | 33.82 | 17.15 |
| 7 | 143.79 | 88.96 | 117.49 | 88.95 | 117.47 | 88.93 | 40.36 | 24.73 |
| 8 | 155.11 | 98.29 | 117.77 | 98.28 | 117.77 | 98.26 | 103.63 | 88.92 |
| 9 | 155.11 | 98.29 | 149.69 | 98.29 | 149.68 | 98.28 | 119.46 | 98.26 |
| 10 | 180.40 | 117.80 | 158.65 | 117.78 | 158.64 | 117.77 | 127.25 | 117.76 |
| 11 | 181.08 | 117.80 | 161.28 | 117.79 | 161.27 | 117.78 | 159.42 | 117.76 |
| 12 | 188.64 | 130.09 | 175.31 | 130.08 | 175.30 | 130.07 | 161.33 | 130.06 |
| 13 | 188.64 | 151.61 | 183.14 | 151.61 | 183.13 | 151.61 | 168.14 | 151.60 |
| 14 | 206.98 | 160.66 | 185.91 | 160.65 | 185.90 | 160.64 | 169.50 | 160.64 |
| 15 | 236.94 | 165.92 | 196.69 | 165.90 | 196.68 | 165.89 | 170.03 | 165.88 |
| 16 | 236.94 | 165.92 | 197.77 | 165.91 | 197.75 | 165.90 | 179.15 | 165.88 |
| 17 | 237.63 | 173.44 | 200.02 | 173.42 | 200.01 | 173.40 | 194.93 | 173.40 |
| 18 | 237.63 | 173.44 | 213.54 | 173.44 | 213.53 | 173.43 | 197.25 | 173.40 |
| 19 | 276.49 | 173.85 | 237.98 | 173.83 | 237.97 | 173.80 | 198.14 | 173.78 |

pendicular ( $a$-type) contributions. These were obtained with the eigenstates from a calculation with the DD potential; the corresponding results computed with the BGLK potential are not shown because they are very similar. The dipole function used, Eq. (5), neglects the interaction between the different monomers; we also used the dipole function of the Van Duijneveldts, ${ }^{23}$ which is a polynomial expansion of the $a b$ initio calculated dipole function of the trimer. The fit that was tabulated in Ref. 23 contains some typographical errors, which have large consequences for the line strengths. Using corrected results, ${ }^{58}$ we found that the dipolar matrix elements over the DVR grid functions differ only by about $10 \%$ from the results obtained with our dipole function. Because the validity of the dipole expansion in Ref. 23 is restricted to the region $-90^{\circ} \leqslant \chi_{\nu} \leqslant+90^{\circ}$ we used the function of Eq. (5).

Looking at Tables III and IV one can observe that the conclusions of Ref. 32 regarding the difference between the two potentials hold for all isotopomers: the BGLK potential yields considerably lower energies for the lower states than the DD potential, too low in comparison with experiment, Table I. For the higher excitations the BGLK potential yields better results. In Table V one can observe that the parallel transitions generally have a much larger line strength than the perpendicular transitions. Obviously, the torsional motions involve much larger variations of the monomer dipoles perpendicular to the trimer plane, i.e., parallel to the $c$-axis, than parallel to the plane. One can understand this from geometrical considerations.

Since the effects of H/D substitutions depend strongly on whether it is an internal (i.e., hydrogen-bonding) proton that is substituted or an external one, we discuss these cases separately.

## A. Effects of hydrogen bonded H/D substitutions

Sequential substitution of deuterium atoms by hydrogen atoms in the three hydrogen bonding positions leads to small
frequency shifts of the levels with respect to the pure species. The experimental data (see Table I) of these trimers show a blue shift of about $1.5 \mathrm{~cm}^{-1}$ for each H/D substitution in the series $d_{6} \rightarrow d_{3} a$. The calculated frequency shifts are practically zero, see Fig. 3. Also the line strengths calculated for all these isotopomers are very similar, which is why only the line strengths of $d_{6}$ are listed in Table V. The reason for these negligible shifts in the calculations is twofold. First, since our model constrains the torsional motions to an axis through the hydrogen bonded protons/deuterons, the effective rotational constants $\hbar^{2} / 2 \Lambda_{\nu}$ of the monomers occurring in the first and most important term of $H^{\text {int }}$ are nearly unchanged by internal H/D substitutions, see Table II. Another contribution to the symmetry breaking comes from the third ( $A-B$ ) term of Eq. (3). However, the effect of the second $(A+B)$ term in Eq. (3) on the energies of the pseudorotational levels is small already, see Table 1 in Ref. 32, and the smallness of $A-B$ for these nearly symmetric tops makes the effect of the third term in $H^{\text {int }}$ practically negligible.

A possible improvement of our model, to make it agree better with the observed (small) blue shifts of about 1.5 $\mathrm{cm}^{-1}$ for each internal H/D substitution, would be to change the directions of the axes of internal rotation so that they no longer pass through the internal protons (deuterons). Actually, there may be a physical justification for this assumption: it is not established that the rotations of the water monomers about the hydrogen bonds in the trimer strictly leave the internal protons in fixed positions. In the equilibrium structure from recent $a b$ initio calculations ${ }^{15,30}$ the hydrogen bonded protons are slightly above/below the trimer plane and, when the trimer tunnels to an equivalent equilibrium structure by a flip of one of the external protons, the internal proton must move through the plane as well. Although there is not a good potential surface available for torsions about different axes, we may test this assumption by

TABLE V. Line strengths [in atomic units $\left(e a_{0}\right)^{2}$ ] and frequencies for the transitions from the lowest two levels of several isotopomers, which may be populated in the experiment (Ref. 53). These results were calculated with the DD potential (BGLK frequencies are given in parentheses), $\mu^{\mathrm{H}_{2} \mathrm{O}}=0.728 \quad e a_{0}$. Line strengths marked with dots are zero by symmetry.

|  | $f \leftarrow i$ | Line strength (\\|) | Line strength ( $\perp$ ) | $\Delta$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $h_{6}$ |  |  |  |  |  |
|  | $2,3 \leftarrow 1$ | $\ldots$ | ... | 19.91 | (13.97) |
|  | $4,5 \leftarrow 1$ | ... | 0.009726 | 59.01 | (44.14) |
|  | $6 \leftarrow 1$ | 0.108419 | $\cdots$ | 81.19 | (62.32) |
|  | $7 \leftarrow 1$ | 0.000080 | $\ldots$ | 160.83 | (143.79) |
|  | $8 \leftarrow 1$ | ... | ... | 165.11 | (181.08) |
|  | $9,10 \leftarrow 1$ | ... | 0.036618 | 171.91 | (155.11) |
|  | $4,5 \leftarrow 2,3$ | 0.063463 | ... | 39.10 | (30.18) |
|  | $6 \leftarrow 2,3$ | ... | 0.000150 | 61.28 | (48.35) |
|  | $7 \leftarrow 2,3$ | ... | 0.013404 | 140.92 | (129.82) |
|  | $8 \leftarrow 2,3$ | ... | $\ldots$ | 145.21 | (167.11) |
|  | $9,10 \leftarrow 2,3$ | 0.056887 | $\ldots$ | 152.00 | (141.15) |
| $d_{4} b$ |  |  |  |  |  |
|  | $2 \leftarrow 1$ | 0.000443 | 0.000000 | 7.23 | (3.83) |
|  | $3 \leftarrow 1$ | 0.000005 | 0.000000 | 24.83 | (20.57) |
|  | $4 \leftarrow 1$ | 0.000000 | 0.005027 | 41.68 | (31.52) |
|  | $5 \leftarrow 1$ | 0.000000 | 0.004715 | 54.72 | (42.84) |
|  | $6 \leftarrow 1$ | 0.100992 | 0.000000 | 67.82 | (51.69) |
|  | $7 \leftarrow 1$ | 0.000000 | 0.011141 | 123.82 | (117.47) |
|  | $8 \leftarrow 1$ | 0.000046 | 0.000000 | 127.48 | (117.77) |
|  | $9 \leftarrow 1$ | 0.023805 | 0.000000 | 158.15 | (149.68) |
|  | $10 \leftarrow 1$ | 0.000000 | 0.001954 | 162.86 | (158.64) |
|  | $3 \leftarrow 2$ | 0.000000 | 0.004247 | 17.60 | (16.74) |
|  | $4 \leftarrow 2$ | 0.000007 | 0.000000 | 34.45 | (27.69) |
|  | $5 \leftarrow 2$ | 0.062194 | 0.000000 | 47.49 | (39.01) |
|  | $6 \leftarrow 2$ | 0.000000 | 0.000438 | 60.59 | (47.86) |
|  | $7 \leftarrow 2$ | 0.046179 | 0.000000 | 116.58 | (113.64) |
|  | $8 \leftarrow 2$ | 0.000000 | 0.005422 | 120.24 | (113.93) |
|  | $9 \leftarrow 2$ | 0.000000 | 0.013651 | 150.91 | (145.85) |
|  | $10 \leftarrow 2$ | 0.008702 | 0.000000 | 155.63 | (154.81) |
| $d_{5} b$ |  |  |  |  |  |
|  | $2 \leftarrow 1$ | 0.000005 | 0.000000 | 4.40 | (1.97) |
|  | $3 \leftarrow 1$ | 0.000016 | 0.000000 | 20.60 | (18.72) |
|  | $4 \leftarrow 1$ | 0.000000 | 0.003879 | 32.18 | (26.06) |
|  | $5 \leftarrow 1$ | 0.000000 | 0.004667 | 44.04 | (33.82) |
|  | $6 \leftarrow 1$ | 0.093691 | 0.000000 | 53.75 | (40.36) |
|  | $7 \leftarrow 1$ | 0.000045 | 0.000000 | 110.36 | (103.63) |
|  | $8 \leftarrow 1$ | 0.000000 | 0.012578 | 116.15 | (108.25) |
|  | $9 \leftarrow 1$ | 0.000000 | 0.009616 | 124.75 | (119.46) |
|  | $10 \leftarrow 1$ | 0.017159 | 0.000000 | 137.42 | (127.25) |
|  | $3 \leftarrow 2$ | 0.000000 | 0.002865 | 16.20 | (16.75) |
|  | $4 \leftarrow 2$ | 0.000000 | 0.000000 | 27.78 | (24.09) |
|  | $5 \leftarrow 2$ | 0.064794 | 0.000000 | 39.64 | (31.86) |
|  | $6 \leftarrow 2$ | 0.000000 | 0.000837 | 49.36 | (38.40) |
|  | $7 \leftarrow 2$ | 0.000000 | 0.007927 | 105.96 | (101.67) |
|  | $8 \leftarrow 2$ | 0.046838 | 0.000000 | 111.75 | (106.29) |
|  | $9 \leftarrow 2$ | 0.000031 | 0.000000 | 120.36 | (117.50) |
|  | $10 \leftarrow 2$ | 0.000000 | 0.010956 | 133.03 | (125.28) |
| $d_{6}$ |  |  |  |  |  |
|  | $2,3 \leftarrow 1$ | $\ldots$ | ... | 7.68 | (5.15) |
|  | $4,5 \leftarrow 1$ | ... | 0.008934 | 25.18 | (17.15) |
|  | $6 \leftarrow 1$ | 0.099157 | ... | 36.61 | (24.73) |
|  | $7 \leftarrow 1$ | 0.000037 | $\ldots$ | 96.14 | (88.92) |
|  | $8,9 \leftarrow 1$ | $\cdots$ | 0.028402 | 107.50 | (98.26) |
|  | $4,5 \leftarrow 2,3$ | 0.079899 | ... | 17.50 | (12.01) |
|  | $6 \leftarrow 2,3$ | ... | 0.000462 | 28.93 | (19.59) |
|  | $7 \leftarrow 2,3$ | $\ldots$ | 0.012366 | 88.46 | (83.77) |
|  | $8,9 \leftarrow 2,3$ | 0.032970 | ... | 99.82 | (93.11) |



FIG. 3. Frequency shifts by hydrogen bonded H/D substitutions, calculated with the DD potential. Experimental data are from Ref. 53. In the "Modified model," described in Sec. IV A, the angles between the axes of internal rotation and the axes connecting the centers of mass are fixed at $3^{\circ}$, instead of the $20^{\circ}$ used in the original model.
moving the directions of the axes of internal rotation away from the vectors through the molecular centers of mass and the internal protons. In our original model the internal rotation axes make an angle of $20^{\circ}$ with the lines connecting the centers of mass; here we change this angle, while keeping the same (DD) potential surface. In Fig. 3, "modified model," one observes that the reduction of this angle to about $3^{\circ}$ yields the correct (nearly linear) frequency shifts upon internal H/D substitution. The frequencies are slightly too high now, in comparison with experiment, ${ }^{53}$ while our original model yields frequencies somewhat too low (even with the DD potential). If, indeed, our modified model is valid this would imply that the water monomers in the trimer rotate nearly around the axes which connect the centers of mass-or, which is almost equivalent, around the $\mathrm{O}-\mathrm{O}$ axes (instead of around the $\mathrm{O}-\mathrm{H}$ bonds).

Viant et al. ${ }^{53}$ assign all of the observed bands to the same transition, from level 1 to level 6 . This is corroborated by our results, which show that this transition has a relatively high parallel line strength (and practically no perpendicular component) and frequencies (with the DD potential) that compare well with the experimental values for the entire series.

## B. Effects of external H/D substitutions

In the series $d_{6}, d_{5} b, d_{4} b$ (or $d_{3} b$ ), and $h_{6}$, where the external deuterons are substituted one by one, we find important changes of the torsional levels (see Fig. 4). For the asymmetric isotopomers, $d_{3} b, d_{4} b$, and $d_{5} b$, the splitting of the levels which are degenerate in the symmetric species [with $\operatorname{PI}\left(C_{3 h}\right)$ irrep labels $k= \pm 1$ and $k= \pm 2$ ], is at least as large as the gap between the levels in the latter species. Note that the frequencies and the line strengths of $d_{3} b$ and $d_{4} b$ are very similar, because they differ only by an internal substitution. Therefore, only the line strengths for $d_{4} b$ are listed in Table V. In spite of these large frequency shifts, the symmetry breaking does not lead to mixing of the parallel and per-


FIG. 4. Quantitative results for the externally H/D substituted water trimers, calculated with the DD potential. The correlation between the different levels (indicated by dotted lines) is based on the line strengths of Table V. The arrows mark the assignments of measured transitions.
pendicular character of the transitions. If a transition has a parallel component the perpendicular component is negligible, and vice versa. The transition $1 \rightarrow 6$ has practically the same line strength for all isotopomers (including the pure species). The transition $2,3 \rightarrow 4,5$ in the pure species remains parallel for all species, but is split into a strong and a weak component (e.g., the transition $2 \rightarrow 5$ and $2 \rightarrow 4$ of $d_{4} b$, respectively). On the other hand, the perpendicular transition $1 \rightarrow 4,5$ is split into two almost equal contributions. The transition between the formerly degenerate levels 2 and 3 obtains a large perpendicular line strength in both externally substituted isotopomers. Since, apparently, the character of the torsional wave functions is fairly well conserved even if there is no symmetry, we may also correlate the higher levels in Fig. 4 on the basis of the calculated transition intensities.

Our results confirm the assignment of Viant et al. ${ }^{53}$ of the 45.9 and $46.5 \mathrm{~cm}^{-1}$ bands which they measured for $d_{3} b$ and $d_{4} b$, namely as hot bands associated with the transition from level 2 to level 5. The transition from level 1 to level 4 has a comparable energy difference but, according to its line strength, is much weaker and perpendicular. The experimental molecular beam conditions are such that level 2 may indeed be populated. The band observed at $97.3 \mathrm{~cm}^{-1}$ for $d_{5} b$ was assigned by Liu et al. ${ }^{52}$ as due to the transition from level 1 to level 7, but according to Table V, this transition
only has a very weak parallel component. We suggest to assign this band as a hot band associated with the transition from level 2 to level 8, which has a large parallel dipole strength and practically the same energy difference.

## V. CONCLUSIONS

Whereas the torsional or pseudorotation tunneling motions in $d_{6}$ and $h_{6}$, and also in $d_{3} a$, exhibit permutational symmetry-they belong to the permutation-inversion group $P I\left(C_{3 h}\right)$-the corresponding levels of the other isotopomers in this study do not. In the Hamiltonian that was previously derived ${ }^{31}$ for these internal motions this symmetry breaking is reflected by two phenomena: (i) the effective rotational constants $\hbar^{2} /\left(2 \Lambda_{\nu}\right)$ of the monomers are no longer equal, and (ii) new terms occur in the kinetic energy operator, which do not appear for the symmetric trimers. These additional terms are proportional to the (small) asymmetry ( $A$ $-B$ ) in the trimer rotational constants $A$ and $B$. One of the consequences of these changes is that the degeneracies in the torsional levels with $\operatorname{PI}\left(C_{3 h}\right)$ irrep labels $k= \pm 1$ and $k$ $= \pm 2$ are lifted.

With this new Hamiltonian the torsional levels of several, experimentally observed, isotopomers were calculated by means of a sinc function DVR method. The frequency shifts caused by substitution of the internal protons/deuterons are much too small, in comparison with the shifts observed experimentally: $1.5 \mathrm{~cm}^{-1}$ for each internal $\mathrm{H} / \mathrm{D}$ substitution. This is a result of the fact that the masses of the internal protons/deuterons have practically no effect on the monomer moments of inertia $\Lambda_{\nu}$, while also the additional $(A-B)$ kinetic energy terms in the Hamiltonian for the internal motions only have a negligible influence on the torsional levels. It is shown, however, that with a change in the directions of the axes of internal rotation our model can reproduce the observed $1.5 \mathrm{~cm}^{-1}$ frequency shifts. This modified model still has to be verified by computation of the potential surface for rotations about these different axes. If it is valid, this would imply that the rotations of the water monomers about the hydrogen bonds in the trimer do not occur about axes through the hydrogen bonding (donor) H/D atoms (or, nearly, about the $\mathrm{O}-\mathrm{H}$ bonds), but rather about axes closer to the $\mathrm{O}-\mathrm{O}$ axes.

Substitution of the external H/D atoms causes a much larger symmetry breaking in the energies of the torsional levels. From the line strengths of different transitions, which were also calculated, we conclude, however, that the transitions conserve their parallel or perpendicular character. With the help of these line strengths we assign all the bands observed for the various water trimer isotopomers. For the most part, this confirms the assignments made by the experimentalists. However, in one case, $d_{5} b$, our results suggest that the observed band corresponds to a different transition, namely from level 2 to level 8 , a hot band.

## ACKNOWLEDGMENTS

The authors thank Paul E. S. Wormer for critical reading of the manuscript and for valuable discussions. Also, stimu-
lating discussions with Mark R. Viant, Mac G. Brown, and Richard J. Saykally are gratefully acknowledged.
${ }^{1}$ T. R. Dyke and J. S. Muenter, J. Chem. Phys. 60, 2929 (1974).
${ }^{2}$ G. T. Fraser, Int. Rev. Phys. Chem. 10, 189 (1991), and references therein.
${ }^{3}$ S. Scheiner, Annu. Rev. Phys. Chem. 45, 23 (1994), and references therein.
${ }^{4}$ J. C. Owicki, B. R. Lentz, A. T. Hagler, and H. A. Scheraga, J. Phys. Chem. 79, 2352 (1975).
${ }^{5}$ P. Habitz, P. Bagus, P. Siegbahn, and E. Clementi, Int. J. Quantum Chem. 23, 1803 (1983).
${ }^{6}$ E. Honegger and S. Leutwyler, J. Chem. Phys. 88, 2582 (1988).
${ }^{7}$ O. Mó, M. Yáñez, and J. Elguero, J. Chem. Phys. 97, 6628 (1992).
${ }^{8}$ N. Pugliano and R. J. Saykally, Science 257, 1937 (1992).
${ }^{9}$ J. G. C. M. van Duijneveldt van de Rijdt and F. B. van Duijneveldt, Chem. Phys. 175, 271 (1993).
${ }^{10}$ W. Klopper and M. Schütz, Chem. Phys. Lett. 237, 536 (1993).
${ }^{11}$ M. Schütz, T. Bürgi, and S. Leutwyler, J. Chem. Phys. 99, 5228 (1993).
${ }^{12}$ D. J. Wales, J. Am. Chem. Soc. 115, 11180 (1993).
${ }^{13}$ D. J. Wales, J. Am. Chem. Soc. 115, 11191 (1993).
${ }^{14}$ S. S. Xantheas and T. H. Dunning, Jr., J. Chem. Phys. 98, 8037 (1993).
${ }^{15}$ S. S. Xantheas and T. H. Dunning, Jr., J. Chem. Phys. 99, 8774 (1993).
${ }^{16}$ J. K. Gregory and D. C. Clary, Chem. Phys. Lett. 228, 547 (1994).
${ }^{17}$ J. K. Gregory, D. J. Wales, and D. C. Clary, J. Chem. Phys. 102, 1592 (1994).
${ }^{18}$ K. Liu, J. G. Loeser, M. J. Elrod, B. C. Host, J. A. Rzepiela, and R. J. Saykally, J. Am. Chem. Soc. 116, 3507 (1994).
${ }^{19}$ K. Liu, M. J. Elrod, J. G. Loeser, J. D. Cruzan, N. Pugliano, M. G. Brown, J. A. Rzepiela, and R. J. Saykally, Faraday Discuss. Chem. Soc. 97, 35 (1994).
${ }^{20}$ S. Suzuki and G. A. Blake, Chem. Phys. Lett. 229, 499 (1994).
${ }^{21}$ S. S. Xantheas, J. Chem. Phys. 100, 7523 (1994).
${ }^{22}$ T. Bürgi, S. Graf, S. Leutwyler, and W. Klopper, J. Chem. Phys. 103, 1077 (1995).
${ }^{23}$ J. G. C. M. van Duijneveldt van de Rijdt and F. B. van Duijneveldt, Chem. Phys. Lett. 237, 560 (1995).
${ }^{24}$ J. E. Fowler and H. F. Schaefer, J. Am. Chem. Soc. 117, 446 (1995).
${ }^{25}$ J. K. Gregory and D. C. Clary, J. Chem. Phys. 102, 7817 (1995).
${ }^{26}$ J. K. Gregory and D. C. Clary, J. Chem. Phys. 103, 8924 (1995).
${ }^{27}$ J. K. Gregory and D. C. Clary, Chem. Phys. Lett. 237, 39 (1995).
${ }^{28}$ W. Klopper, M. Schütz, H. P. Lüthi, and S. Leutwyler, J. Chem. Phys. 103, 1085 (1995).
${ }^{29}$ D. Sabo, Z. Bačić, T. Bürgi, and S. Leutwyler, Chem. Phys. Lett. 244, 283 (1995).
${ }^{30}$ S. S. Xantheas, J. Chem. Phys. 102, 4505 (1995).
${ }^{31}$ A. van der Avoird, E. H. T. Olthof, and P. E. S. Wormer, J. Chem. Phys. 105, 8034 (1996).
${ }^{32}$ E. H. T. Olthof, A. van der Avoird, P. E. S. Wormer, K. Liu, and R. J. Saykally, J. Chem. Phys. 105, 8051 (1996).
${ }^{33}$ J. D. Cruzan, M. G. Brown, K. Liu, L. B. Braly, and R. J. Saykally, J. Chem. Phys. 105, 6634 (1996).
${ }^{34}$ J. D. Cruzan, L. B. Braly, K. Liu, M. G. Brown, J. G. Loeser, and R. J. Saykally, Science 271, 59 (1996).
${ }^{35}$ J. K. Gregory and D. C. Clary, J. Phys. Chem. 100, 18014 (1996).
${ }^{36}$ J. K. Gregory and D. C. Clary, J. Chem. Phys. 105, 6626 (1996).
${ }^{37}$ K. Liu, M. G. Brown, C. Carter, R. J. Saykally, J. K. Gregory, and D. C. Clary, Nature (London) 381, 501 (1996).
${ }^{38}$ K. Liu, J. D. Cruzan, and R. J. Saykally, Science 271, 929 (1996).
${ }^{39}$ K. Liu, M. G. Brown, J. D. Cruzan, and R. J. Saykally, Science 271, 62 (1996).
${ }^{40}$ D. J. Wales and T. R. Walsh, J. Chem. Phys. 105, 6957 (1996).
${ }^{41}$ T. R. Walsh and D. J. Wales, J. Chem. Soc., Faraday Trans. 92, 2505 (1996).
${ }^{42}$ J. D. Cruzan, M. R. Viant, M. G. Brown, and R. J. Saykally, J. Phys. Chem. 101, 9022 (1997).
${ }^{43}$ J. D. Cruzan, Ph.D. thesis, University of Berkeley, 1997.
${ }^{44}$ O. Engkvist, N. Forsberg, M. Schutz, and G. Karlström, Mol. Phys. 90, 277 (1997).
${ }^{45}$ J. K. Gregory, D. C. Clary, K. Liu, M. G. Brown, and R. J. Saykally, Science 275, 814 (1997).
${ }^{46}$ J. K. Gregory and D. C. Clary, J. Phys. Chem. 101, 6813 (1997).
${ }^{47}$ K. Liu, M. G. Brown, and R. J. Saykally, J. Phys. Chem. 101, 8995 (1997).
${ }^{48}$ K. Liu, M. G. Brown, J. D. Cruzan, and R. J. Saykally, J. Phys. Chem. 101, 9011 (1997).
${ }^{49}$ D. J. Wales, J. Chem. Phys. 106, 7193 (1997).
${ }^{50}$ D. Sabo, Z. Bačić, S. Graf, and S. Leutwyler, Chem. Phys. Lett. 261, 318 (1996).
${ }^{51}$ J. M. Sorenson, J. K. Gregory, and D. C. Clary, Chem. Phys. Lett. 263, 680 (1996).
${ }^{52}$ K. Liu, M. G. Brown, M. R. Viant, J. D. Cruzan, and R. J. Saykally, J. Phys. Chem. 89, 1373 (1996).
${ }^{53}$ M. R. Viant, J. D. Cruzan, D. D. Lucas, M. G. Brown, K. Liu and R. J. Saykally, J. Phys. Chem. 101, 9032 (1997).
${ }^{54}$ H. Hönl and F. London, Z. Phys. 33, 803 (1925).
${ }^{55}$ R. N. Zare, Angular Momentum (Wiley, New York, 1988).
${ }^{56}$ D. T. Colbert and W. H. Miller, J. Chem. Phys. 96, 1982 (1992).
${ }^{57}$ G. C. Groenenboom and D. T. Colbert, J. Chem. Phys. 99, 9681 (1993).
${ }^{58}$ F. B. van Duijneveldt (private communication).
${ }^{59}$ M. R. Viant, J. D. Cruzan, M. G. Brown, R. J. Saykally, A van der Avoird, and M. Geleijns, J. Chem. Phys. (submitted).

