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Intra- and Intermolecular Rovibrational States of HCl-H\textsubscript{2}O and DCl-H\textsubscript{2}O Dimers from Full-Dimensional and Fully Coupled Quantum Calculations\(^\dagger\)

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We report full-dimensional and fully coupled quantum bound-state calculations of the \(J=1\) intra- and intermolecular rovibrational states of two isotopologues of the hydrogen chloride-water dimer, HCl-H\textsubscript{2}O (HH) and DCl-H\textsubscript{2}O (DH). The present study complements our recent theoretical investigations of the \(J=0\) nine-dimensional (9D) vibrational level structure of these and two other H/D isotopologues of this noncovalently bound molecular complex, and employs the same accurate 9D permutation invariant polynomial-neural network potential energy surface. The calculations yield all intramolecular vibrational fundamentals of the HH and DH dimers and the low-energy intermolecular rovibrational states in these intramolecular vibrational manifolds. The results are compared with those of the 9D \(J=0\) calculations of the same dimers. The energy differences between the \(K=1\) and \(K=0\) eigenstates exhibit pronounced variations with the intermolecular rovibrational states, for which a qualitative explanation is provided.

Key words: Weakly bound dimers, Rovibrational states, Quantum calculations

I. INTRODUCTION

Small hydrogen-bonded clusters of hydrogen chloride and water molecules have for decades been the subject of experimental and theoretical investigations [1]. This intense interest has been driven mainly by the opportunity that these clusters present for studying the fundamental aspects of important chemical processes in the atmosphere, ozone depletion being one of them. Moreover, clusters of hydrogen chloride with a variable number of water molecules afford a unique microscopic view of the first steps of hydration that ultimately result in the dissociation of HCl in bulk water [1, 2].

As the elementary constituent of the prototypical acid-water system, the hydrogen chloride–water dimer has particular importance. Consequently, it has been the focus of numerous high-resolution spectroscopic studies, that include microwave spectroscopy [3, 4], ragout-jet FTIR [5, 6] and infrared (IR) cavity ringdown spectroscopy [7] in the gas phase, and IR spectroscopy in liquid helium, as well as in nanodroplets [8–12]. The most investigated isotopologue has been the HCl-H\textsubscript{2}O dimer. Its vibrational predissociation dynamics upon the excitation of the HCl stretch fundamental was studied experimentally [13, 14], leading to the determination of the dimer dissociation energy \(D_0=1334\pm10\ \text{cm}^{-1}\) [13]. Some partially or fully deuterated isotopologues

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of the hydrogen chloride–water dimer have been probed experimentally as well, by IR (DCl–D$_2$O) [6, 7] and microwave spectroscopies (DCl–H$_2$O, HCl–D$_2$O, DCl–D$_2$O [3], and analogous isotopologues involving HDO). These experimental investigations have been complemented by a variety of theoretical treatments. From the electronic structure calculations over the years [15–19], it emerged that the HCl–H$_2$O dimer has the equilibrium structure with a near-linear hydrogen bond, in which HCl acts as the proton donor to the O atom of water as the proton acceptor. The geometry of this global minimum is non-planar, leading to two symmetrically equivalent pyramidal C$_s$ structures (see FIG. 3 in Ref.[20]). A significant contribution to the theoretical description of the HCl-H$_2$O dimer was made by Mancini and Bowman [21], in the form of the ab initio based nine-dimensional (9D) potential energy surface (PES) of the dimer based on a permutationally invariant fit to over 44,000 CCSD(T)-F12b/aug-cc-pVTZ configurations and energies. This PES was used in the full-dimensional quantum diffusion Monte Carlo (DMC) calculations, which for the dimer’s dissociation energy ($D_0$) gave the value of 1348±3 cm$^{-1}$, in good agreement with the experimental result [13]. What was still lacking at this point was a rigorous full-dimensional quantum calculations of the coupled excited inter- and intramolecular (ro)vibrational levels of the HCl-H$_2$O dimer.

This missing link was provided by our recently published theoretical study [20], which had two goals. One of them was introducing a new full-dimensional (9D) PES of the HCl-H$_2$O dimer, designated PES-2021, based on circa 43,000 data points computed at the level of CCSD(T)-F12a/aug-cc-pVTZ with the basis-set superposition-error (BSSE) correction. The ab initio points were fit utilizing the ultraflexible permutation invariant polynomial-neural network (PIP-NN) approach [22–24]. The other goal was to present the first fully coupled 9D quantum calculations of the inter- and intramolecular vibrational states of the HCl-H$_2$O (HH) dimer, performed on PES-2021. These calculations characterized the vibrationally averaged non-planar ground-state geometry of the HCl-H$_2$O dimer, the intramolecular vibrational fundamentals of both monomers, and their frequency shifts relative to the gas-phase monomer values, together with the low-energy intermolecular vibrational states in each of the intramolecular vibrational manifolds and the manifestations of the coupling between the two sets of modes [20]. The properties calculated for the HCl-H$_2$O dimer turned out to be in excellent agreement with the spectroscopic data for the dimer in the literature. The dimer binding energy computed in 9D, $D_0=1334.63$ cm$^{-1}$, agrees extremely well with the experimental $D_0$ equal to 1334±10 cm$^{-1}$ [13]. In addition, the ground-state expectation value of the out-of-plane bend angle of H$_2$O, 33.80°, and the HCl stretch frequency shift, −157.9 cm$^{-1}$, both from 9D calculations on PES-2021, are in very good accord with the corresponding experimental values for the dimer, 34.7° for the bend angle [4] and −161.9 cm$^{-1}$ for the redshift of the HCl stretch fundamental [5, 7].

In the follow-up work [25], the rigorous full-dimensional investigation of the HH dimer in Ref.[20] was extended to three isotopologues of the hydrogen chloride-water dimer: DCl-H$_2$O (DH), HCl-D$_2$O (HD), and DCl-D$_2$O (DD). Its goal was to reveal the isotopologue variations of several bound-state properties of the hydrogen chloride-water dimer, and compare them to those of the HH dimer. These calculations also employed 9D PES-2021, and the same highly efficient fully coupled 9D quantum bound-state methodology. For the isotopologues in question, they yielded all intramolecular vibrational fundamentals, and their frequency shifted relative to the isolated monomer values, in combination with the low-lying intermolecular vibrational states in each of the intramolecular vibrational manifolds of interest. Moreover, for each isotopologue, important vibrationally averaged intermolecular geometric properties were computed for the dimer in the ground vibrational state, as well as the three rotational constants.

What enabled the extremely demanding 9D quantum bound-state calculations in the above studies is the methodology developed by us in Ref.[26]. It is the adaptation of the general approach for fully coupled quantum computation of intra- and intermolecular (ro)vibrational excitations of noncovalently bound molecular complexes [27] to weakly bound triatomic dimers. The exceptional effectiveness of this methodology has two main sources. One of them is the surprising insight [27, 28] that fully coupled calculation of high-frequency intramolecular vibrational excitations in noncovalently bound systems can be accomplished by utilizing compact final basis sets with only a small number of low-lying intermolecular eigenstates whose ener-
ies are far below those of the intramolecular vibrational states of interest. This was rationalized by making a physically motivated assumption of extremely weak coupling between the intramolecular vibrational fundamentals and overtones and the very highly excited intermolecular states close in energy [27, 28]. Consequently, excluding the latter from the basis has no effect on the accuracy of the results. This results in a large reduction of the dimension of the basis set employed.

The other key factor is the computational strategy designed specifically to exploit the above insight. The full (ro)vibrational Hamiltonian of the dimer [20, 25–27, 29], 9D in the case of HCl-H\(_2\)O and the isotopologues, is partitioned into four terms: a (5D) rigid-monomer intramolecular vibrational Hamiltonian, two intramolecular vibrational Hamiltonians—one for the triatom (water) monomer (3D) and the other for the diatom (hydrogen chloride) moiety (1D), and a 9D remainder term. Each of the three reduced-dimension Hamiltonians is diagonalized separately and small portions of their low-energy eigenstates are included in a compact (9D) product contracted basis that covers all internal, intra- and intermolecular, degrees of freedom (DOFs) of the dimer. It is only because of the use of the contracted eigenstate basis for the intermolecular vibrational DOFs that fully coupled 9D quantum bound-state calculations of all intramolecular vibrational fundamentals of the noncovalently bound triatom-diatom complexes are possible. It enables straightforward selection of just a small number of lowest-energy intermolecular vibrational eigenstates for inclusion in the compact final 9D product contracted basis [27], in which the full (ro)vibrational Hamiltonian of the dimer is diagonalized.

The use of the eigenstates of reduced-dimension Hamiltonians to decrease the size of the final full-dimensional basis is not entirely new. Baćić and Light introduced the sequential diagonalization-truncation scheme [30–33], that proved very successful in the applications to fluxional molecules and molecular complexes such as LiCN/LiNC, HCN/HNC, (HF)\(_2\) [34], (HCl)\(_2\) [35], and others. For polyatomic molecules such as acetylene, H\(_2\)O\(_2\), CH\(_4\), and CH\(_3\)\(^+\), Carter and Handy [36] and Carrington and co-workers [37, 38], implemented similar ideas of dividing the internal coordinates into two groups and using the eigenvectors of the corresponding reduced-dimension Hamiltonians in the final product contracted basis. In addition, monomer vibrational eigenstates of noncovalently bound complexes have been used as the contracted basis for the intramolecular vibrational DOFs of the complexes [39]. But, the basis for the intermolecular DOFs was not contracted in these studies. This omission precluded the possibility of a straightforward major reduction in the size of the intermolecular vibrational basis (and therefore of the full product contracted basis) described above.

Other successful, and very challenging, applications of the methodology outlined above are the following: rigorous 8D quantum calculations of the intramolecular stretch fundamentals and frequency shifts of two H\(_2\) molecules in the large clathrate hydrate cage [40], the fully coupled 9D quantum treatment of the intra- and intermolecular vibrational levels of H\(_2\)O in (rigid) C\(_{60}\) [41], and the fully coupled 9D quantum calculations of flexible H\(_2\)O/HDO intramolecular excitations and intermolecular states of the benzene-H\(_2\)O and benzene-HDO complexes (for rigid benzene), together with their IR and Raman spectra [42].

The bound state calculations of the hydrogen chloride–water dimer so far [20, 25] were performed for total angular momentum \(J=0\). In this paper we present rigorous full-dimensional quantum calculations of the coupled intra- and intermolecular rovibrational states of the HH and DH isotopologues for total angular momentum \(J=1\). As before [20, 25], the accurate 9D PIP-NN PES-2021 is employed. The \(J=1\) rovibrational states are calculated using a slightly modified version of methodology used by us previously to compute in 9D the \(J=0\), 1 rovibrational levels of H\(_2\)O/D\(_2\)O-CO [26] and HDO-CO [29]. The computed eigenstates encompass all intramolecular vibrational fundamentals of the dimers, together with the low-lying intermolecular rovibrational states within each intramolecular vibrational manifold. Particular attention is given to the dependence of the energies of the intermolecular rovibrational states on the (approximate) quantum number \(K\), the projection of \(J\) on the intermolecular axis of the dimer, that is important for characterizing the nature of the rovibrational states.

II. COMPUTATIONAL METHODOLOGY

In a previous work on H\(_2\)O-CO and D\(_2\)O-CO [26], we presented a general method to compute the rovibrational levels of a water-diatom complex in full (9D) dimensionality. We make use of the same method in this study with only one significant modification pertaining
to the exploitation of nuclear-exchange symmetry, as described below in Sections II.C and II.E.

A. Rovibrational Hamiltonian and coordinates

The procedure starts with the rovibrational Hamiltonian of the water-hydrogen chloride dimer, as obtained from the general, weakly-bound-dimer expression presented by Brocks et al. [43]

$$\hat{H}(\mathbf{Q}, \mathbf{q}_A, r_B, \Omega) = \hat{T}_{\text{rot}}(\mathbf{Q}, \Omega) + \hat{T}_v(\mathbf{q}_A) + \hat{T}_r(\mathbf{q}_A, \mathbf{q}_B) + V(\mathbf{Q}, \mathbf{q}_A, r_B)$$

In Eq.(1), \(Q \equiv (r_0, \alpha_A, \beta_B)\) denotes the collection of intermolecular coordinates: \(r_0\) is the distance from the center of mass (c.m.) of the water moiety to that of the hydrogen-chloride moiety, \(\alpha_A \equiv (\alpha_A, \beta_A, \gamma_A)\) denotes the three Euler angles that fix the orientation of a cartesian frame attached to the water moiety (which we label BF\(_A\)) relative to one attached to the dimer (which we label DF), and \(\beta_B \equiv (\alpha_B, \beta_B)\) denotes the two Euler angles that fix the orientation of the HCl internuclear vector \((r_B, \hat{z}_D)\), which points from the Cl nucleus to the H nucleus) relative to DF. \(\Omega \equiv (\alpha, \beta)\) denotes the Euler angles that orient the \(z\) axis of the DF frame \((\hat{z}_D)\) relative to a space-fixed axis system (SF). \(\mathbf{q}_A \equiv (R_1, R_2, \Theta)\) denotes the Radau coordinates [44–46] that we take as the water moiety’s vibrational coordinates, and \(r_B \equiv |r_B|\) is the vibrational coordinate of the hydrogen-chloride moiety.

The origin of the DF frame is at the c.m. of the dimer, with \(\hat{z}_D\) taken to be parallel to the vector \((\hat{r}_0)\) pointing from the water c.m. to the hydrogen-chloride c.m. The BF\(_A\) (water-moiety) frame is centered at the water c.m. with axes defined by Radau, bisector-\(z\) embedding [47]: \(\hat{z}_A\) is parallel to \(\hat{r}_1 + \hat{r}_2\) (\(\hat{r}_i\) is the unit vector parallel to the \(\bf R_i\) Radau vector), \(\hat{y}_A\) is parallel to \(\hat{R}_1 \times \hat{R}_2\), and \(\hat{x}_A = \hat{y}_A \times \hat{z}_A\).

\(\hat{T}_{\text{rot}}\), the rotational/intermolecular-kinetic-energy operator in Eq.(1), is given by [43]

$$\hat{T}_{\text{rot}}(\mathbf{Q}, \Omega) = -\frac{1}{2\mu_0} \frac{\partial^2}{\partial r_0^2} + B_0(r_0)(\hat{j}^2 - \cot \beta \frac{\partial}{\partial \beta}) - 2\hat{J} \cdot (\hat{j}_A + \hat{j}_B) + \hat{j}_A^2 + \hat{j}_B^2 + 2\hat{J} \cdot \hat{j}_B$$

where \(\mu_0\) is the dimer’s reduced mass, \(B_0(r_0) \equiv 1/(2\mu_0 r_0^2)\), \(\hat{J}\) is the vector operator corresponding to the rotational angular momentum of the dimer measured with respect to the DF frame, and \(\hat{j}_A\) and \(\hat{j}_B\) are the vector operators corresponding, respectively, to the rotational angular momenta of the water and hydrogen-chloride moieties measured with respect to the DF frame.

\(\hat{T}_v\) and \(\hat{T}_r\), the rotation-vibration kinetic-energy operators of the water and hydrogen-chloride monomers, respectively, can be expressed as

$$\hat{T}_v(\mathbf{q}_A) = \hat{T}_v^A(\mathbf{q}_A) + \hat{T}_v^B(\mathbf{q}_A) + \hat{T}_{\text{cor}}(\mathbf{q}_A)$$

with \(\hat{T}_v^A\), \(\hat{T}_v^B\), and \(\hat{T}_{\text{cor}}\) given respectively by Eqs.(4), (5), and (6) of Ref.[26] (as adapted from Ref.[47]), and

$$\hat{T}_r(\mathbf{q}_A, \mathbf{q}_B) = \hat{T}_r^A(\mathbf{q}_A, \mathbf{q}_B) + \hat{T}_r^B(\mathbf{q}_A, \mathbf{q}_B)$$

with \(\hat{T}_r^A\) and \(\hat{T}_r^B\) given, respectively, by Eq.(9) and Eq.(10) of Ref.[26].

Finally, \(V(\mathbf{Q}, \mathbf{q}_A, r_B)\), the 9D potential-energy function in Eq.(1), is taken to be the water-hydrogen chloride potential PES-2021 from Ref.[20]. Note that the dimer potential is independent of the individual values of \(\alpha_A\) and \(\alpha_B\) and is dependent only on their difference \(\bar{\alpha} \equiv \alpha_A - \alpha_B\) (\(e.g.,\ see Appendix B of Ref.[39]). We denote this dependence by defining the five “reduced” intermolecular coordinates \(\hat{Q} \equiv (r_0, \bar{\alpha}, \beta_A, \gamma_A, \beta_B)\). One sees that \(V\) is a function of nine coordinates, as expected for the PES associated with a five-atom system.

B. General approach to computing the eigenstates of \(\hat{H}\)

In order to solve for the eigenstates of \(\hat{H}\) we first divide it into four terms, three reduced-dimension Hamiltonians and a remainder term:

$$\hat{H} = \hat{H}_{\text{rot}}(\mathbf{Q}, \Omega) + \hat{H}_v(\mathbf{q}_A) + \hat{H}_r(\mathbf{q}_A, \mathbf{q}_B) + \Delta \hat{H}(\mathbf{Q}, \mathbf{q}_A, r_B)$$

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In this equation the “rotational-intermolecular Hamiltonian” is defined as
\[
\hat{H}_{\text{inter}}^{\text{rot}} = T_{\text{inter}}(\mathbf{Q}, \Omega) + \hat{T}_r^A(\omega_A, \mathbf{q}_A^0) + T_B^r(\omega_B, r_B^0) + V_{\text{inter}}(\mathbf{Q})
\] (6)
where \(\mathbf{q}_A^0 = (R_A^0, r_B^0, \Theta^0)\) represents fixed values for the three vibrational coordinates of the water moiety, \(r_B^0\) is a fixed value for the hydrogen-chloride vibrational coordinate, and
\[
V_{\text{inter}}(\mathbf{Q}) = V(\mathbf{Q}, \mathbf{q}_A^0, r_B^0)
\] (7)
The vibrational Hamiltonian for the water moiety is defined as
\[
\hat{H}_v^A(\mathbf{q}_A) = T_v^A(\mathbf{q}_A) + V^A(\mathbf{q}_A)
\] (8)
where
\[
V^A(\mathbf{q}_A) = V(\mathbf{Q}^\infty, \mathbf{q}_A, r_B^0)
\] (9)
and \(\mathbf{Q}^\infty\) denotes fixed values of the reduced intermolecular coordinates corresponding to a large value of the inter-monomer distance (more on this in Section II.D). \(\hat{H}_v^B\), the vibrational Hamiltonian for the hydrogen-chloride moiety, is defined as
\[
\hat{H}_v^B(r_B) = T_v^B(r_B) + V^B(r_B)
\] (10)
where
\[
V^B(r_B) = V(\mathbf{Q}^0, \mathbf{q}_A^0, r_B)
\] (11)
and \(\mathbf{Q}^0\) denotes fixed values of the reduced intermolecular coordinates (more on this in Section II.D). Finally, the remainder term in Eq.(5) is given by
\[
\Delta \hat{H}(\mathbf{Q}, \mathbf{q}_A, r_B) = [\hat{T}_r^A(\omega_A, \mathbf{q}_A) - \hat{T}_r(\omega_A, \mathbf{q}_A^0)] + \hat{T}_r^\text{con}(\omega_A, \mathbf{q}_A) + [\hat{T}_r^B(\omega_B, r_B) - \hat{T}_r(\omega_B, r_B^0)] + \Delta V(\mathbf{Q}, \mathbf{q}_A, r_B)
\] (12)
where
\[
\Delta V(\mathbf{Q}, \mathbf{q}_A, r_B) \equiv V(\mathbf{Q}, \mathbf{q}_A, r_B) - V_{\text{inter}}(\mathbf{Q}) - V^A(\mathbf{q}_A) - V^B(r_B)
\] (13)

Second, we solve for the lowest-energy eigenstates of the reduced Hamiltonians \(\hat{H}_{\text{inter}}^{\text{rot}}, \hat{H}_v^A, \) and \(\hat{H}_v^B\). We denote the set of such eigenstates of \(\hat{H}_{\text{inter}}^{\text{rot}}\) for a particular value of the rotational angular-momentum quantum number \(J\) as \(|\kappa, J\rangle\), \(\kappa = 1, \ldots, N_{\text{inter}}\). Those corresponding to \(\hat{H}_v^A\) we denote as \(|\nu_A\rangle\), where \(\nu_A \equiv (v_1, v_2, v_3)\) represents the set of three quantum numbers (symmetric-stretch, bend, asymmetric-stretch) specifying the water-moiety vibrational state. And, we denote those corresponding to \(\hat{H}_v^B\) as \(|\nu_B\rangle\), where \(\nu_B\) is the HCl vibrational quantum number.

Finally, we construct a set of 9D basis states for a given value of \(J\) consisting of products of the form
\[
|\kappa, J; \nu_A; \nu_B\rangle \equiv |\kappa, J\rangle |\nu_A\rangle |\nu_B\rangle
\] (14)
and diagonalize the matrix of \(\hat{H}\) expressed in this basis. Since the matrix elements of \(\hat{H}_{\text{inter}}^{\text{rot}}, \hat{H}_v^A, \) and \(\hat{H}_v^B\) in this basis are trivially obtained, the major effort in solving for the eigenstates of \(\hat{H}\) involves the computation of the matrix elements of \(\Delta \hat{H}\).

C. Calculation of the \(J=1\) eigenstates of \(\hat{H}_{\text{inter}}^{\text{rot}}\)

The procedure used here to calculate the \(J=1\) eigenstates of \(\hat{H}_{\text{inter}}^{\text{rot}}\) is largely the same as that outlined in Sec.2.2 of Ref.[25]. That is, we employ the Chebyshev version of filter diagonalization to diagonalize matrices of the operator in symmetry-specific bases constructed from the primitive basis functions [48]
\[
|s, j_A, k_A, m, j_B; JK\rangle \equiv |r_{0,s}\rangle |j_A, k_A, m\rangle |j_B, K-m\rangle |JK\rangle
\] (15)
with \(J=1\) and \(K=1, 0, 1\). In Eq.(15), \(|r_{0,s}\rangle\) denotes one of 20 functions associated with a potential-optimized discrete variable representation (PODVR) [49, 50] covering the \(r_0\) coordinate (for details see Sec.3.1.2 of Ref.[20]), \(|j_A, k_A, m\rangle\) \((j_A=0, \ldots, 10)\), denotes a symmetric-top eigenfunction covering the \(\omega_A\) coordinates, \(|j_B, K-m\rangle\) \((j_B=0, \ldots, 18)\) denotes a spherical harmonic function covering the \(\omega_B\) coordinates, and \(|JK\rangle\) is a normalized “little-d” Wigner matrix element
\[
|JK\rangle \equiv \sqrt{\frac{2J+1}{2}} d_{JK}^d(\beta)
\] (16)
As in Ref.[25], we choose the \(\mathbf{q}_A^0\) and \(r_B^0\) values required to obtain \(V_{\text{inter}}\) (see Eq.(7)) so as to correspond, respectively, to a water moiety with OH bond distances of 0.96 Å and a bond angle of 104.52°, and a hydrogen-chloride moiety with a bond distance of 1.3097 Å. This rigid-water geometry is very close to the equilibrium geometry of the free monomer [51]. The HCl bond distance is slightly longer than the expectation value of the computed ground state of \(\hat{H}_v^B\).

The only substantive difference in this work from that
of Sec.2.2 of Ref.[25] is that here we make full use of the G4 symmetry of the HH and DH dimers to block-diagonalize the $\hat{H}^{\text{rot}}_{\text{inter}}$ matrix for a given species into four blocks. That is, in addition to symmetrizing the basis functions with respect to inversion (as in Ref.[25]), we also symmetrize them with respect to exchange of the H nuclei of the water. The former was accomplished by using Eq.(31) of Ref.[25] to obtain a random state function of definite parity with which to initiate the filter-diagonalization procedure. The latter was accomplished by including the functions in Eq.(15) with only even or only odd values of $k_A$ in that random initial state function. As a result, for each isotopologue four different filter-diagonalization runs—one for each $G_4$ irreducible representation ("irrep")—were carried out to obtain all the $|\kappa, J\rangle$.

For the para $(k_A\text{ even})$/ortho $(k_A\text{ odd})$ runs a total of $793,700/784,800$ functions in Eq.(15) contributed to the basis. The number of independent basis functions associated with a given irrep block is about a factor of two smaller than these numbers due to the parity-filtering employed to produce the initial state function for that block.

D. Calculation of the eigenstates of $\hat{H}^A$ and $\hat{H}^B$

The eigenstates of $\hat{H}^A$ and $\hat{H}^B$ were computed in this work in a manner identical to the procedures employed in Ref.[25]. As such, we refer the reader to that work for details. Here, we simply point out that the $Q^\infty$-coordinate values used to obtain $V^A$ (see Eq.(9)) were chosen to be those associated with the planar, $C_{2v}$ dimer geometry with $r_0=26.5$ Å. Thus, the computed $|v_A\rangle$ are essentially isolated-water vibrational states. In contrast, the $Q^9$-coordinate values required to obtain $V^B$ (see Eq.(11)) were chosen to be the expectation values of the $Q$ for the ground state of $\hat{H}^{\text{rot}}_{\text{inter}}$ for $J=0$. Hence, the eigenstates of $\hat{H}^B$ are those corresponding to a “dimer-adapted” HCl (DCl) potential. We made this choice for the hydrogen-chloride moiety because of the information from experiment indicating a significant perturbation of that moiety upon dimerization with water [5, 7].

E. Calculation of the eigenstates of $\hat{H}$

The $J=1$ eigenstates of $\hat{H}$ were computed in this work by a procedure almost identical to that described in Sec.II E of Ref.[26]. The only substantive procedural difference from the latter work is that here we fully block-diagonalize the $\hat{H}$ matrix into the four blocks associated with the $G_4$ irreps, whereas in Ref.[26] we limited the block diagonalization to just two parity-specific blocks and thus neglected to use all of the ortho/para symmetry information available. We chose to make fuller use of symmetry in this work owing to the considerably larger 9D basis sets that we employ here relative to those used previously.

Explicit incorporation of ortho/para symmetry into the 9D basis is somewhat more involved than incorporating parity into that basis. The parity of the 9D basis function $|\kappa, J; v_A; v_B\rangle$ is entirely determined by the parity of the intermolecular eigenstate $|\kappa, J\rangle$. Hence, to obtain even- (odd-) parity eigenfunctions of $\hat{H}$ one simply includes only even- (odd-) parity $|\kappa, J\rangle$ in constructing one’s 9D basis. In contrast, the symmetry of a 9D basis function with respect to H exchange is determined by the way in which both $|\kappa, J\rangle$ and $|v_A\rangle$ transform upon H exchange. Denoting the exchange operation as (12), then

$$
(12)|\kappa, J; v_A; v_B\rangle = (12)|\kappa, J\rangle \times |v_A\rangle \times |v_B\rangle = \sigma_{\kappa, J}\sigma_{v_A}|\kappa, J; v_A; v_B\rangle
$$

where $\sigma_{\kappa, J}=\pm 1$ and $\sigma_{v_A}=\pm 1$ are, respectively, the eigenvalues of $|\kappa, J\rangle$ and $|v_A\rangle$ with respect to the (12) operator. Thus, both ortho and para $|\kappa, J\rangle$ states contribute to the same symmetry block of the $\hat{H}$ matrix, as do both ortho and para $|v_A\rangle$ states.

With the above in mind, we now outline the calculation and diagonalization of the symmetry-specific $\hat{H}$ matrices. We start with a set of parity-specific 9D basis functions containing both ortho and para members. We proceed to compute, per Sections II E 1–3 of Ref.[26], the matrix elements of $\Delta \hat{H}$ in the set of states $|\kappa, J; \eta; \xi\rangle$, where $|\eta\rangle$ and $|\xi\rangle$ denote the DVR basis functions that contribute to the eigenstates of $\hat{H}^A$ and $\hat{H}^B$, respectively. We then calculate the matrix elements of $\hat{H}$,

$$
\langle \kappa', J; \eta'; \xi'| \hat{H} |\kappa, J; \eta; \xi\rangle = (E_{\kappa, J} + E_{v_A} + E_{v_B})\delta_{\kappa, \kappa'}\delta_{\eta, \eta'}\delta_{\xi, \xi'} + \sum_{\eta, \eta', \xi, \xi'} \left( \langle \eta'| \langle \eta|v_A\rangle \langle \eta'| \eta\rangle \langle \eta'| |v_B\rangle \langle \eta'| |\xi\rangle \right) \langle \kappa', J; \eta'; \xi'| \Delta \hat{H} |\kappa, J; \eta; \xi\rangle
$$

for the para 9D basis states and diagonalize that matrix by direct diagonalization. $E_{\kappa, J}$, $E_{v_A}$, and $E_{v_B}$ are the eigenvalues of $|\kappa, J; v_A; v_B\rangle$ with respect to $\hat{H}^{\text{rot}}_{\text{inter}}$. DOI:10.1063/1674-0068/cjcp2110189 ©2021 Chinese Physical Society
ular states, but now in the ortho states (up to 920 cm$^{-1}$ above the ground state). For DH all the $\hat{H}^{\text{rot}}_{\text{inter}}$ eigenstates up to about 850 cm$^{-1}$ above the ground state were included. In all cases (for both isotopologues and for each $G_1$-irrep block of the $\hat{H}$ matrix) the total number of basis states corresponding to each block thus amounted to 14,700.

### III. RESULTS AND DISCUSSION

Selected low-energy $J=1$, $K=0$ and $J=1$, $K=1$ intermolecular states of the HH and DH isotopologues from the 9D calculations, for the monomers in their ground vibrational states, are presented in Tables I and II, respectively. Their assignments in terms of the fundamentals, overtones, and combinations of three intermolecular modes, $\nu_{\text{inversion}}$, $\nu_{\text{stretch}}$, and $\nu_{\text{rock}}$, are explained in Ref.[20]. It is evident that the $K=1$ intermolecular states are closely spaced doublets (to within a fraction of a wavenumber) and, strictly speaking, the label $K$ stands for the absolute value $|K|$. Comparison of the $J=1$, $K=0$ states of the HH and DH dimers in Tables I and II, respectively, with the corresponding $J=0$ states of the two isotopologues (Table I in Ref.[25]) shows that they differ in energy by at most 0.5 cm$^{-1}$.

The same 9D $J=1$, $K=0$ and $J=1$, $K=1$ intermolecular states, but now in the $\nu_2$, $\nu_{1\text{HC}}$ ($\nu_{2\text{DC}}$), $\nu_1$ and $\nu_3$ intramolecular vibrational manifolds, respectively, are shown in Tables III–VI for the HH dimer and in Tables VII–X for the DH dimer. In all instances, the energy differences between $J=1$, $K=0$ states reported here and the corresponding previously calculated $J=0$ states (Tables VII and VIII in Ref.[25]) do not exceed 0.5 cm$^{-1}$. This means that the observations made earlier [20, 25] regarding the significant effects of the intramolecular vibrational excitations of the monomers on the $J=0$ intermolecular states are closely spaced doublets (to within a fraction of a wavenumber) and, strictly speaking, the label $K$ stands for the absolute value $|K|$. Comparison of the $J=1$, $K=0$ states of the HH and DH dimers in Tables I and II, respectively, with the corresponding previously calculated $J=0$ states of the two isotopologues (Table I in Ref.[25]) shows that they differ in energy by at most 0.5 cm$^{-1}$.

The same 9D $J=1$, $K=0$ and $J=1$, $K=1$ intermolecular states, but now in the $\nu_2$, $\nu_{1\text{HC}}$ ($\nu_{2\text{DC}}$), $\nu_1$ and $\nu_3$ intramolecular vibrational manifolds, respectively, are shown in Tables III–VI for the HH dimer and in Tables VII–X for the DH dimer. In all instances, the energy differences between $J=1$, $K=0$ states reported here and the corresponding previously calculated $J=0$ states (Tables VII and VIII in Ref.[25]) do not exceed 0.5 cm$^{-1}$. This means that the observations made earlier [20, 25] regarding the significant effects of the intramolecular vibrational excitations of the monomers on the $J=0$ intermolecular states are closely spaced doublets (to within a fraction of a wavenumber) and, strictly speaking, the label $K$ stands for the absolute value $|K|$. Comparison of the $J=1$, $K=0$ states of the HH and DH dimers in Tables I and II, respectively, with the corresponding previously calculated $J=0$ states of the two isotopologues (Table I in Ref.[25]) shows that they differ in energy by at most 0.5 cm$^{-1}$.

### Table I Low-energy $J=1$ intermolecular rovibrational states of the HH dimer in the manifold of the intramolecular vibrational ground state from 9D calculations.

| Intermolecular state | $|K|$ | $\Delta E^a$ | irrep | BSN |
|----------------------|------|-------------|------|-----|
| Ground state         | 0    | 0.000       | $A_u$ | 0.9927 |
|                      | 1    | 13.736      | $B_u$ | 0.9925 |
|                      | 1    | 13.740      | $B_g$ | 0.9925 |
| $\nu_{\text{inversion}}$ | 0    | 85.444      | $B_g$ | 0.9931 |
|                      | 1    | 94.653      | $A_g$ | 0.9923 |
|                      | 1    | 94.794      | $A_u$ | 0.9924 |
| $\nu_{\text{stretch}}$ | 0    | 131.817     | $A_u$ | 0.9855 |
|                      | 1    | 145.586     | $B_u$ | 0.9792 |
|                      | 1    | 145.590     | $B_g$ | 0.9852 |
| $\nu_{\text{rock}}$  | 0    | 145.893     | $B_u$ | 0.9883 |
|                      | 1    | 164.269     | $A_g$ | 0.9932 |
|                      | 1    | 164.481     | $A_u$ | 0.9933 |
| $2\nu_{\text{inversion}}$ | 0    | 217.157     | $B_u$ | 0.9919 |
|                      | 1    | 222.299     | $B_u$ | 0.9925 |
|                      | 1    | 222.322     | $B_g$ | 0.9925 |
| $\nu_{\text{inversion}} + \nu_{\text{stretch}}$ | 0    | 217.534     | $B_g$ | 0.9853 |
|                      | 1    | 226.469     | $A_g$ | 0.9849 |
|                      | 1    | 226.612     | $A_u$ | 0.9849 |

$^a$ $\Delta E$ is a state’s energy in cm$^{-1}$ relative to that of the $J=1$ ground state of the dimer.

### Table II Low-energy $J=1$ intermolecular rovibrational states of the DH dimer in the manifold of the intramolecular vibrational ground state from 9D calculations.

| Intermolecular state | $|K|$ | $\Delta E^a$ | irrep | BSN |
|----------------------|------|-------------|------|-----|
| Ground state         | 0    | 0.000       | $A_u$ | 0.9949 |
|                      | 1    | 13.732      | $B_u$ | 0.9948 |
|                      | 1    | 13.734      | $B_g$ | 0.9948 |
| $\nu_{\text{inversion}}$ | 0    | 84.043      | $B_g$ | 0.9957 |
|                      | 1    | 92.882      | $A_g$ | 0.9953 |
|                      | 1    | 92.924      | $A_u$ | 0.9954 |
| $\nu_{\text{stretch}}$ | 0    | 133.374     | $A_u$ | 0.9917 |
|                      | 1    | 147.154     | $B_u$ | 0.9915 |
|                      | 1    | 147.162     | $B_g$ | 0.9915 |
| $\nu_{\text{rock}}$  | 0    | 138.753     | $B_u$ | 0.9956 |
|                      | 1    | 156.099     | $A_g$ | 0.9950 |
|                      | 1    | 156.139     | $A_u$ | 0.9950 |
| $2\nu_{\text{inversion}}$ | 0    | 217.712     | $B_g$ | 0.9955 |
|                      | 1    | 215.931     | $B_g$ | 0.9955 |
|                      | 1    | 215.931     | $B_g$ | 0.9955 |
| $\nu_{\text{inversion}} + \nu_{\text{stretch}}$ | 0    | 217.712     | $B_g$ | 0.9924 |
|                      | 1    | 226.339     | $A_g$ | 0.9921 |
|                      | 1    | 226.430     | $A_u$ | 0.9922 |

$^a$ $\Delta E$ is a state’s energy in cm$^{-1}$ relative to that of the $J=1$ ground state of the dimer.
TABLE III Low-energy $J=1$ intermolecular rovibrational states of the HH dimer in the $\nu_2$ intramolecular vibrational manifold from 9D calculations.

| Intermolecular state | $|K|$ | $\Delta E^a$/cm$^{-1}$ | irrep | BSN |
|----------------------|------|------------------------|-------|-----|
| Ground state         | 0    | 0.000                  | $A_u$ | 0.9872 |
|                      | 1    | 13.847                 | $B_u$ | 0.9868 |
|                      | 1    | 13.850                 | $B_g$ | 0.9868 |
| $\nu_{\text{inversion}}$ | 0    | 93.492                | $B_g$ | 0.9897 |
|                      | 1    | 102.281               | $A_g$ | 0.9896 |
|                      | 1    | 102.388               | $A_u$ | 0.9897 |
| $\nu_{\text{stretch}}$ | 0    | 131.478               | $A_u$ | 0.9799 |
|                      | 1    | 145.359               | $B_u$ | 0.9782 |
|                      | 1    | 145.363               | $B_g$ | 0.9795 |
| $\nu_{\text{rock}}$ | 0    | 147.216               | $B_u$ | 0.9884 |
|                      | 1    | 166.083               | $A_g$ | 0.9892 |
|                      | 1    | 166.228               | $A_u$ | 0.9894 |
| $2\nu_{\text{inversion}}$ | 0    | 232.477               | $A_u$ | 0.9867 |
|                      | 1    | 236.952               | $B_u$ | 0.9869 |
|                      | 1    | 236.968               | $B_g$ | 0.9869 |
| $\nu_{\text{inversion}}+\nu_{\text{stretch}}$ | 0    | 225.216               | $B_g$ | 0.9815 |
|                      | 1    | 233.680               | $A_g$ | 0.9815 |
|                      | 1    | 233.817               | $A_u$ | 0.9816 |

$^a\Delta E$ is a state’s energy relative to that of the lowest-energy $J=1$ state in the $\nu_2$ manifold. The latter is at an energy of 1595.782 cm$^{-1}$ relative to the $J=1$ ground state of the dimer.

The analogous results in Table XII for the DH dimer are very similar.

These significant variations of $E_{J=1,|K|=1} - E_{J=1, K=0}$ with the intermolecular vibrational states can be rationalized as follows, starting with those for the inversion mode. The positions of the H atoms of H$_2$O largely determine the magnitude of the A rotational constant and thus $E_{J=1,|K|=1} - E_{J=1, K=0}$. In our treatment [20], the deviation of the H$_2$O moiety from the planar $C_{2v}$ geometry of the complex is described by $\beta_A$, the water polar angle between the $C_2$ axis of H$_2$O and the vector connecting the c.m. of H$_2$O to that of HCl. The expectation value of $\beta_A$, and therefore the non-planarity of the complex, increases markedly (relative to the ground-state value) for $\nu_{\text{inversion}}$, and even more for $2\nu_{\text{inversion}}$ [20]. This results in the decrease of the A rotational constant, and hence $E_{J=1,|K|=1} - E_{J=1, K=0}$, in going from the intermolecular ground state to $\nu_{\text{inversion}}$ and $2\nu_{\text{inversion}}$. Exciting $\nu_{\text{rock}}$ also increases $\beta_A$, but much less than $\nu_{\text{inversion}}$ [20]. Moreover, this increase in $\beta_A$ occurs roughly within O–HCl plane [20]. Apparently, this brings the H atoms of water closer (on the average)
to the O−Cl heavy-atom axis, thereby increasing the A rotational constant and $E_{J=1,|K|=1} - E_{J=1,|K|=0}$.

The above also explains why for a given intermolecular state of either HH or DH dimer, the variation of $E_{J=1,|K|=1} - E_{J=1,|K|=0}$ (relative to value in the ground intramolecular state) for different intramolecular vibrational states is much weaker.

Finally, we discuss briefly the last column in Tables I−X labeled BSN, for basis-set norm. The entries in this column measure the contribution of the dominant product inter/intra-basis state to the given 9D eigenstate. For the majority of states shown, the BSN is close to 1, meaning that these eigenstates are highly “pure”, i.e., dominated by a single inter/intra-basis state. But there are some exceptions. For many of the states in Tables IV and VIII, belonging to the $\nu_{\text{HCl}}$ and $\nu_{\text{DCl}}$ intramolecular vibrational manifolds, respectively, the BSNs are considerably smaller than 1, as low as 0.6−0.7, indicating rather strong basis-state mixing. This was already noted for the $J=0$ states of the HH dimer [20], and is consistent with the observation that the $\nu_{\text{HCl}}$ and $\nu_{\text{DCl}}$ modes couple most strongly to the intermolecular vibrational modes of the dimers [20, 25].

Small BSNs can also arise from the coupling between $K=1$ intermolecular vibrational states belonging to two different intramolecular vibrational manifolds. We have two examples of this. In Table VI, in the $\nu_2$ intramolecular vibrational manifold of the HH dimer, two $K=1$ $\nu_{\text{stretch}}$ states of $A_g$ symmetry arise from such a coupling, leading to a splitting of the “pure” $K=1$ state and small BSNs. In addition, in Table IX, for the DH dimer, the same type of coupling splits both members of the $|K|=1$ doublet of the ground intermolecular state in the $\nu_2$ intramolecular vibrational manifold.

The energies of the $J=1$ intramolecular vibrational levels of the HH and DH dimer from the 9D calculations differ negligibly from those of their $J=0$ counterparts reported previously [20, 25]. Therefore, the detailed discussion in Refs. [20] and [25] regarding the $J=0$ intramolecular vibrational eigenstates and their frequency shifts relative to the isolated monomer values applies.
from our 9D calculations for the HH dimer [20], while the HCl/DCl stretch frequency shift in the dimers, as previously [20, 25], the fractional vibrational frequency shifts of these results that was not addressed previously. This quantity is defined as $\Delta \nu_{\text{HCl}}$. Consequently, $\Delta \nu_{\text{HCl}}/\nu_{\text{HCl,free}} = 0.054$. Thus, the two fractional vibrational frequency shifts $\Delta \nu_{\text{HCl}}/\nu_{\text{HCl,free}}$ and $\Delta \nu_{\text{DCI}}/\nu_{\text{DCI,free}}$ are nearly identical, remarkably unaffected by the H/D isotopic substitution. This is consistent with the prediction of the simple theory due to Buckingham, based on the first- and second-order perturbation theory, of the effects of solvent molecules on the intramolecular stretch frequency of a solute diatomic molecule [52, 53].

### IV. CONCLUSION

We have presented the results of the full-dimensional and fully coupled quantum calculations of the intra- and intermolecular rovibrational states of the HH and DH dimers for total angular momentum $J=1$. This extends our recent rigorous studies of the $J=0$ 9D coupled inter- and intramolecular vibrational eigenstates of these two dimers, as well as two other H/D isotopologues of the hydrogen chloride-water dimer [20, 25]. The accurate 9D PIP-NN PES-2021 developed in Ref. [20] is employed in this work, together with the slight modification of the sophisticated and highly efficient bound-state methodology that we used earlier to compute the 9D $J=0$, 1 rovibrational states of $\text{H}_2\text{O}/\text{D}_2\text{O}-\text{CO}$ [26] and HDO–CO [29].

The results include all intramolecular vibrational fundamentals of the dimers, in combination with the low-

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**Table VII** Low-energy $J=1$ intermolecular rovibrational states of the DH dimer in the $v_2$ intramolecular vibrational manifold from 9D calculations.

| Intermolecular state | $|K|$ | $\Delta E^a$/cm$^{-1}$ | irrep | BSN  |
|----------------------|------|---------------------|-------|------|
| Ground state         | 0    | 0.000               | $A_u$ | 0.9872 |
|                      | 1    | 13.813              | $B_u$ | 0.9869 |
|                      | 1    | 13.814              | $B_g$ | 0.9869 |
| $v_{\text{inversion}}$ | 0    | 92.374              | $B_g$ | 0.9900 |
|                      | 1    | 100.638             | $A_g$ | 0.9905 |
|                      | 1    | 100.663             | $A_u$ | 0.9906 |
| $v_{\text{stretch}}$  | 0    | 133.082             | $A_u$ | 0.9830 |
|                      | 1    | 146.941             | $B_u$ | 0.9827 |
|                      | 1    | 146.949             | $B_g$ | 0.9828 |
| $v_{\text{rock}}$     | 0    | 139.991             | $B_u$ | 0.9889 |
|                      | 1    | 157.971             | $A_g$ | 0.9884 |
|                      | 1    | 157.987             | $A_u$ | 0.9885 |
| $2v_{\text{inversion}}$ | 0    | 227.405             | $A_u$ | 0.9873 |
|                      | 1    | 229.533             | $B_g$ | 0.9850 |
|                      | 1    | 229.534             | $B_u$ | 0.9850 |
| $v_{\text{inversion}}+v_{\text{stretch}}$ | 0    | 225.578             | $B_g$ | 0.9860 |
|                      | 1    | 233.593             | $A_g$ | 0.9864 |
|                      | 1    | 233.676             | $A_u$ | 0.9865 |

$^a$ $\Delta E$ is a state’s energy relative to that of the lowest-energy $J=1$ state in the $v_2$ manifold. The latter is at an energy of 1594.967 cm$^{-1}$ relative to the $J=1$ ground state of the dimer.

**Table VIII** Low-energy $J=1$ intermolecular rovibrational states of the DH dimer in the $v_{\text{DCI}}$ intramolecular vibrational manifold from 9D calculations.

| Intermolecular state | $|K|$ | $\Delta E^a$/cm$^{-1}$ | irrep | BSN  |
|----------------------|------|---------------------|-------|------|
| Ground state         | 0    | 0.000               | $A_u$ | 0.6447 |
|                      | 1    | 14.826              | $B_u$ | 0.7738 |
|                      | 1    | 14.835              | $B_g$ | 0.7718 |
| $v_{\text{inversion}}$ | 0    | 72.700              | $B_g$ | 0.9333 |
|                      | 1    | 82.682              | $A_g$ | 0.8992 |
|                      | 1    | 82.757              | $A_u$ | 0.8997 |
| $v_{\text{stretch}}$  | 0    | 137.681             | $B_u$ | 0.5852 |
|                      | 1    | 151.047             | $B_g$ | 0.7254 |
|                      | 1    | 151.055             | $B_g$ | 0.7273 |
| $v_{\text{rock}}$     | 0    | 150.407             | $B_u$ | 0.7886 |
|                      | 1    | 167.059             | $A_g$ | 0.9346 |
|                      | 1    | 167.126             | $A_u$ | 0.9347 |
| $2v_{\text{inversion}}$ | 0    | 208.865             | $A_u$ | 0.9021 |
|                      | 1    | 212.907             | $B_g$ | 0.5317 |
|                      | 1    | 212.955             | $B_g$ | 0.5657 |
| $v_{\text{inversion}}+v_{\text{stretch}}$ | 0    | 211.162             | $B_g$ | 0.8357 |
|                      | 1    | 220.687             | $A_g$ | 0.8058 |
|                      | 1    | 220.942             | $A_u$ | 0.8095 |

$^a$ $\Delta E$ is a state’s energy relative to that of the lowest-energy $J=1$ state in the $v_{\text{DCI}}$ manifold. The latter is at an energy of 1977.511 cm$^{-1}$ relative to the $J=1$ ground state of the dimer.
The energy difference $E_{J=1,|K|=1} - E_{J=1,|K|=0}$ is explained by considering the perturbation of the ground state by the excited state. These variations are explained qualitatively by considering how the excitation of each mode affects the vibration averaged positions of the $H$ atoms of water, which in turn change the magnitude of the $A$ rotational constant of the dimer and thus the difference $E_{J=1,|K|=1} - E_{J=1,|K|=0}$. In a few

**Note:** $\Delta E$ is a state's energy in cm$^{-1}$ relative to that of the lowest-energy $J=1$ state in the $\nu_3$ manifold. The latter is at an energy of 3750.273 cm$^{-1}$ relative to the $J=1$ ground state of the dimer.

**Table IX** Low-energy $J=1$ intermolecular rovibrational states of the DH dimer in the $\nu_2$ intramolecular rovibrational manifold from 9D calculations.

| Intermolecular state | $|K|$ | $\Delta E^a$ | irrep | BSN |
|----------------------|------|-------------|-------|-----|
| Ground state         | 0    | 0.000       | $A_u$ | 0.9737 |
|                      | 1    | 13.070      | $B_u$ | 0.9238 |
|                      | 1    | 13.543      | $B_u$ | 0.6936 |
|                      | 1    | 13.076      | $B_g$ | 0.3012 |
|                      | 1    | 13.548      | $B_g$ | 0.6863 |
| $\nu_{inversion}$    | 0    | 77.074      | $B_g$ | 0.9898 |
|                      | 1    | 86.660      | $A_g$ | 0.9813 |
|                      | 1    | 86.103      | $A_u$ | 0.9813 |
| $\nu_{stretch}$      | 0    | 133.497     | $A_u$ | 0.9750 |
|                      | 1    | 147.214     | $B_u$ | 0.7405 |
|                      | 1    | 147.221     | $B_g$ | 0.7394 |
| $\nu_{rock}$         | 0    | 137.411     | $B_u$ | 0.9771 |
|                      | 1    | 154.071     | $A_g$ | 0.9768 |
|                      | 1    | 154.118     | $A_u$ | 0.9420 |
| $2\nu_{inversion}$   | 0    | 203.208     | $A_u$ | 0.9806 |
|                      | 1    | 206.895     | $B_u$ | 0.9772 |
|                      | 1    | 206.898     | $B_g$ | 0.9770 |
| $\nu_{inversion} + \nu_{stretch}$ | 0   | 211.491     | $B_g$ | 0.9570 |
|                      | 1    | 220.260     | $A_g$ | 0.9716 |
|                      | 1    | 220.358     | $A_u$ | 0.9718 |

$^a \Delta E$ is a state's energy in cm$^{-1}$ relative to that of the lowest-energy $J=1$ state in the $\nu_3$ manifold. The latter is at an energy of 3750.273 cm$^{-1}$ relative to the $J=1$ ground state of the dimer.

**Table X** Low-energy $J=1$ intermolecular rovibrational states of the DH dimer in the $\nu_3$ intramolecular rovibrational manifold from 9D calculations.

| Intermolecular state | $|K|$ | $\Delta E^a$ | irrep | BSN |
|----------------------|------|-------------|-------|-----|
| Ground state         | 0    | 0.000       | $B_u$ | 0.9902 |
|                      | 1    | 13.580      | $A_0$ | 0.9898 |
|                      | 1    | 13.582      | $A_g$ | 0.9898 |
| $\nu_{inversion}$    | 0    | 75.600      | $B_g$ | 0.9719 |
|                      | 1    | 84.658      | $B_u$ | 0.9727 |
| $\nu_{stretch}$      | 0    | 133.026     | $B_u$ | 0.9849 |
|                      | 1    | 146.637     | $A_0$ | 0.9836 |
|                      | 1    | 146.643     | $A_g$ | 0.9834 |
| $\nu_{rock}$         | 0    | 136.802     | $A_0$ | 0.9848 |
|                      | 1    | 153.927     | $B_g$ | 0.9699 |
|                      | 1    | 153.964     | $B_u$ | 0.9701 |
| $2\nu_{inversion}$   | 0    | 200.222     | $B_u$ | 0.9847 |
|                      | 1    | 203.945     | $A_g$ | 0.9628 |
|                      | 1    | 203.959     | $A_u$ | 0.9312 |
| $\nu_{inversion} + \nu_{stretch}$ | 0   | 209.464     | $A_g$ | 0.9712 |
|                      | 1    | 218.272     | $B_g$ | 0.9674 |
|                      | 1    | 218.368     | $B_u$ | 0.9695 |

**Table XI** Average $E_{J=1,|K|=1} - E_{J=1,|K|=0}$ energy differences for selected low-energy intermolecular states in the DH dimer. They are based on the results shown in Tables I–VI.

| $S_0^a$ | $\nu_2$ | $\nu_1$ | $\nu_3$ | $\nu_{DCI}$ |
|---------|---------|---------|---------|-------------|
| Ground state | 13.738 | 13.849 | 13.442 | 13.586 | 13.279 |
| $\nu_{inversion}$ | 9.280 | 8.843 | 9.338 | 9.352 | 10.388 |
| $\nu_{stretch}$ | 13.771 | 13.883 | 13.485 | 13.615 | 13.883 |
| $\nu_{rock}$ | 18.482 | 18.940 | 17.870 | 18.382 | 16.782 |
| $2\nu_{inversion}$ | 5.155 | 4.483 | 5.486 | 5.474 | 4.483 |

$^a$ $S_0$ refers to the ground state.

**Table XII** Average $E_{J=1,|K|=1} - E_{J=1,|K|=0}$ energy differences for selected low-energy intermolecular states in the DH dimer. They are based on the results shown in Tables II–X.

| $S_0^a$ | $\nu_2$ | $\nu_1$ | $\nu_3$ | $\nu_{DCI}$ |
|---------|---------|---------|---------|-------------|
| Ground state | 13.733 | 13.814 | 13.309 | 13.581 | 14.831 |
| $\nu_{inversion}$ | 8.860 | 8.277 | 9.008 | 9.038 | 10.020 |
| $\nu_{stretch}$ | 13.876 | 13.863 | 13.821 | 13.614 | 13.370 |
| $\nu_{rock}$ | 17.366 | 17.988 | 16.684 | 17.144 | 16.686 |
| $2\nu_{inversion}$ | 3.148 | 2.129 | 3.688 | 3.730 | 4.666 |

$^a$ $S_0$ refers to the ground state.
instances, the coupling between $K=1$ intermolecular vibrational states belonging to two different intramolecular vibrational manifolds results in fine splitting of certain $K=1$ states.

Finally, we demonstrate that the HCl and DCI stretch fundamentals in the HH and DH dimers, respectively, have virtually identical fractional vibrational frequency shifts, in accord with the prediction of the simple perturbative treatment by Buckingham of the solvent-induced frequency shifts of diatomic solutes [52, 53].

The calculations in this paper, together with the earlier ones of the 9D $J=0$, 1 rovibrational states of H$_2$O/D$_2$O–CO [26] and HDO–CO [29], demonstrate the maturity and the versatility of our methodology for full-dimensional and fully coupled quantum calculations of the rovibrational eigenstates of noncovalently bound diatom-triatom molecular complexes, for both the ground and excited intramolecular vibrational states of the monomers.

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[1] A. K. Samanta, Y. Wang, J. S. Mancini, J. M. Bowman, and H. Reisler, Chem. Rev. 116, 4913 (2016).
[2] R. P. de Tudela and D. Marx, Phys. Rev. Lett. 119, 223001 (2017).
[3] A. C. Legon and L. C. Willoughby, Chem. Phys. Lett. 95, 449 (1983).
[4] Z. Kisiel, B. A. Pietrewicz, P. W. Fowler, A. C. Legon, and E. Steiner, J. Phys. Chem. A 104, 6970 (2000).
[5] M. Weimann, M. Farnik, and M. A. Suhm, Phys. Chem. Chem. Phys. 4, 3933 (2002).
[6] M. Farnik, M. Weimann, and M. A. Suhm, J. Chem. Phys. 118, 10120 (2003).
[7] A. J. Honeycutt, R. J. Strickland, F. Hellberg, and R. J. Saykally, J. Chem. Phys. 118, 1223 (2003).
[8] M. Ortlieb, Ō. Birer, M. Letzner, G. D. Schwaab, and M. Havenith, J. Phys. Chem. A 111, 12192 (2007).
[9] D. Skvortsov, S. J. Lee, M. Y. Choi, and A. F. Vilesov, J. Phys. Chem. A 113, 7360 (2009).
[10] S. D. Flynn, D. Skvortsov, A. M. Morrison, T. Liang, M. Y. Choi, G. E. Douberly, and A. F. Vilesov, J. Phys. Chem. Lett. 1, 2233 (2010).
[11] A. M. Morrison, S. D. Flynn, T. Liang, and G. E. Douberly, J. Phys. Chem. A 114, 8090 (2010).
[12] M. Letzner, S. Gruen, D. Habig, K. Hanke, T. Endres, P. Nieto, G. Schwaab, L. Walewski, M. Wollenhaupt, H. Forbert, D. Marx, and M. Havenith, J. Chem. Phys. 139, 154304 (2013).
[13] B. E. Casterline, A. K. Moller, L. C. Ch’ng, and H. Reisler, J. Phys. Chem. A 114, 9774 (2010).
[14] A. K. Samanta, L. C. Ch’ng, and H. Reisler, Chem. Phys. Lett. 575, 1 (2013).
[15] M. J. Packer and D. C. Clary, J. Phys. Chem. 99, 14323 (1995).
[16] S. Re, Y. Osamura, Y. Suzuki, and H. F. Schaefer III, J. Chem. Phys. 109, 973 (1998).
[17] G. M. Chaban, R. B. Gerber, and K. C. Janda, J. Phys. Chem. A 105, 8323 (2001).
[18] M. E. Alikhani and B. Silvi, Phys. Chem. Chem. Phys. 5, 2494 (2003).
[19] M. Masia, H. Forbert, and D. Marx, J. Phys. Chem. A 111, 12181 (2007).
[20] Y. Liu, J. Li, P. M. Felker, and Z. Bačić, Phys. Chem. Chem. Phys. 23, 7101 (2021).
[21] J. S. Mancini and J. M. Bowman, J. Chem. Phys. 138, 121102 (2013).
[22] B. Jiang, J. Li, and H. Guo, Int. Rev. Phys. Chem. 35, 479 (2016).
[23] B. Jiang and H. Guo, J. Chem. Phys. 139, 054112 (2013).
[24] J. Li, B. Jiang, and H. Guo, J. Chem. Phys. 139, 204103 (2013).
[25] P. M. Felker, Y. Liu, J. Li, and Z. Bačić, J. Phys. Chem. A 125, 6437 (2021).
[26] P. M. Felker and Z. Bačić, J. Chem. Phys. 153, 074107 (2020).
[27] P. M. Felker and Z. Bačić, J. Chem. Phys. 151, 024305 (2019).
[28] D. Lauvergnat, P. M. Felker, Y. Scribano, D. M. Benoit, and Z. Bačić, J. Chem. Phys. 150, 154303 (2019).
[29] P. M. Felker and Z. Bačić, J. Phys. Chem. A 125, 980 (2021).
[30] Z. Bačić and J. C. Light, J. Chem. Phys. 85, 4594 (1986).
[31] Z. Bačić and J. C. Light, J. Chem. Phys. 86, 3065 (1987).
[32] Z. Bačić, R. M. Whitnell, D. Brown, and J. C. Light, Comput. Phys. Commun. 51, 35 (1988).
[33] Z. Bačić and J. C. Light, Annu. Rev. Phys. Chem. 40, 469 (1989).
[34] D. H. Zhang, Q. Wu, J. Z. H. Zhang, M. von Dirke, and Z. Bačić, J. Chem. Phys. 102, 2315 (1995).
[35] Y. Qiu and Z. Bačić, J. Chem. Phys. 106, 2158 (1997).
[36] S. Carter and N. C. Handy, Comput. Phys. Commun. 51, 49 (1988).

DOI:10.1063/1674-0068/cjcp2110189 ©2021 Chinese Physical Society
[37] X. G. Wang and T. Carrington Jr., J. Chem. Phys. 119, 101 (2003).
[38] X. G. Wang and T. Carrington Jr., J. Chem. Phys. 129, 234102 (2009).
[39] X. G. Wang and T. Carrington, J. Chem. Phys. 148, 074108 (2018).
[40] P. M. Felker, D. Lauvergnat, Y. Scribano, D. M. Benoit, and Z. Bačić, J. Chem. Phys. 151, 124311 (2019).
[41] P. M. Felker and Z. Bačić, J. Chem. Phys. 152, 014108 (2020).
[42] P. M. Felker and Z. Bačić, J. Chem. Phys. 152, 124103 (2020).
[43] G. Brocks, A. van der Avoird, B. T. Sutcliffe, and J. Tennyson, Molec. Phys. 50, 1025 (1983).
[44] B. R. Johnson and W. P. Reinhardt, J. Chem. Phys. 85, 4538 (1986).
[45] Z. Bačić, D. Watt, and J. C. Light, J. Chem. Phys. 89, 947 (1988).
[46] B. T. Sutcliffe and J. Tennyson, Int. J. Quantum Chem. 39, 183 (1991).
[47] X. G. Wang and T. Carrington, J. Chem. Phys. 146, 104105 (2017).
[48] X. G. Wang and T. Carrington Jr., J. Chem. Phys. 134, 044313 (2011).
[49] J. Echave and D. C. Clary, Chem. Phys. Lett. 190, 225 (1992).
[50] H. Wei and T. Carrington Jr., J. Chem. Phys. 97, 3029 (1992).
[51] A. R. Hoy and P. R. Bunker, J. Mol. Spectrosc. 74, 1 (1979).
[52] A. D. Buckingham, Proc. Roy. Soc. A 248, 169 (1958).
[53] A. D. Buckingham, Trans. Faraday Soc. 56, 753 (1960).