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Overtone vibrational spectroscopy in H₂-H₂O complexes: A combined high level theoretical *ab initio*, dynamical and experimental study

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First results are reported on overtone ($\nu_{\text{OH}} = 2 \leftarrow 0$) spectroscopy of weakly bound H₂-H₂O complexes in a slit supersonic jet, based on a novel combination of (i) vibrationally mediated predissociation of H₂-H₂O, followed by (ii) UV photodissociation of the resulting H₂O, and (iii) UV laser induced fluorescence on the nascent OH radical. In addition, intermolecular dynamical calculations are performed in full 5D on the recent *ab initio* intermolecular potential of Valiron *et al.* [J. Chem. Phys. **129**, 134306 (2008)] in order to further elucidate the identity of the infrared transitions detected. Excellent agreement is achieved between experimental and theoretical spectral predictions for the most strongly bound van der Waals complex consisting of ortho ($I = 1$) H₂ and ortho ($I = 1$) H₂O (oH₂-oH₂O). Specifically, two distinct bands are seen in the oH₂-oH₂O spectrum, corresponding to internal rotor states in the upper vibrational manifold of Σ and Π rotational character. However, none of the three other possible nuclear spin modifications (pH₂-oH₂O, pH₂-pH₂O, or oH₂-pH₂O) are observed above current signal to noise level, which for the pH₂ complexes is argued to arise from displacement by oH₂ in the expansion mixture to preferentially form the more strongly bound species. Direct measurement of oH₂-oH₂O vibrational predissociation in the time domain reveals lifetimes of 15(2) ns and <5(2) ns for the Σ and Π states, respectively. Theoretical calculations permit the results to be interpreted in terms of near resonant energy levels and intermolecular alignment of the H₂ and H₂O wavefunctions, providing insight into predissociation dynamical pathways from these metastable levels. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4732581>]

I. INTRODUCTION

The potential energy surface that mediates collisional interactions between common chemical reactants and products such as H₂ and H₂O can be relatively shallow,¹ but nevertheless plays a critical role in a wide variety of chemical physics from interstellar cosmochemistry² to combustion processes.³ Such intermolecular attractions can lead to formation of van der Waals complexes when a sample is cooled to low enough temperatures to stabilize clusters. Since formation of dimers represents the first step in aggregation to larger clusters and ultimately condensation, study of such species offers insight into intermolecular interactions relevant from gas-phase to condensed phase regimes.^{4–6} In particular, bimolecular clusters encompass a variety of noncovalent bonding prototypes, ranging from pure van der Waals interactions⁷ in Ar-Ar ($D_0 \approx 84 \text{ cm}^{-1}$) to the significantly stronger hydrogen bonding in water dimer ($D_0 \approx 1105(10) \text{ cm}^{-1}$).^{8–10} A striking feature of these weakly bound van der Waals systems is the propensity for each component to retain a significant fraction of monomeric character, for example, as noted in the small

shifts of infrared transition frequencies upon complexation.¹¹ Furthermore, weak potential coupling can lead to nearly free internal rotation of the dimer subunits; in Ar-H₂O, for example, the internal rotational spacings are shifted by only a few wavenumbers¹² from those of free H₂O.

As a result, bimolecular clusters have served as a focus of intense theoretical¹³ and experimental¹⁴ work over the years. These species are particularly attractive from a theoretical point of view because there is often weak coupling between intramolecular and intermolecular degrees of freedom. Thus, for an N atom cluster, the quite challenging and often intractable problem of performing *ab initio* and exact quantum nuclear dynamics calculations in full $3N - 6$ internal coordinates can often be instead treated by reduced dimensionality schemes,¹⁵ whereby intramolecular vibrations are assumed to be independent of the cluster size. To a good approximation, this leads to a much simpler Hamiltonian described only by the dimer intermolecular coordinates, which are 5D for the specific complex of interest (i.e., H₂-H₂O) and 6D at the very most. Though still challenging, it is now feasible to solve

theoretically for eigenvalues and eigenfunctions of the complex, a process often limited by the quality of *ab initio* potentials available in full or partial dimensionality.

In the rare cases where high quality *ab initio* potentials for the complex are available in full dimensionality, one can hope to achieve even higher levels of rigor and benchmarking accuracy. Specifically, one can perform full quantum dynamical calculations for monomers in the complex, and then extract an improved intermolecular dimer potential by averaging the *full dimensionality* potential over the intramolecular wavefunctions for a given pair of monomeric (electronic, vibrational) eigenstates. By repeating this procedure for both ground and vibrationally excited states of the complex, one can now make first principles predictions sufficiently accurate for benchmark comparison between theory and high resolution experimental spectroscopy.

The current work focuses on spectroscopy, dynamics, and interaction potentials for $\text{H}_2 + \text{H}_2\text{O}$,^{1,13,15–21} which proves to be relevant in a wide range of terrestrial and extraterrestrial venues.^{2,22–26} In high temperature H_2/O_2 combustion, for example, collisions of the highly energized product H_2O molecules with H_2 reactant provide an important mechanism for heat flow as well as establishing local thermodynamic equilibrium in the flames.³ As a result, there is a broad set of energy dependent cross sections and temperature dependent kinetic rates for such processes at the state-to-state level that prove critical in achieving the desired optimal combustion efficiency.^{22,23,27} The number of such potential pathways under typical high temperature combustion conditions is enormous, far too large to be tackled via detailed state-to-state measurement efforts. On the other hand, many of the desired energy transfer and collisional properties can be calculated from first principles, based on knowledge of a sufficiently accurate potential energy surface in high dimensionality.^{24,26,28–30} The need for high level predictive understanding for such high pressure/temperature combustion phenomena is clearly important, which in turn depends pivotally on benchmark accuracy of the full 9D potential $\text{H}_2 + \text{H}_2\text{O}$ energy surface.^{1,15,17,20–23}

Of particular interest in the interstellar medium (ISM) is the corresponding weakly bound complex, $\text{H}_2\text{-H}_2\text{O}$, due in part to predominance of atomic and molecular hydrogen in the universe.³¹ Indeed, certain regions of the ISM depleted in deep ultraviolet radiation tend to have appreciable concentrations of H_2 molecules rather than H atoms,³² which can in fact trigger chemical synthesis into higher molecular weight species.³³ In conjunction with appreciable concentrations of H_2O , this implies a relatively high probability for $\text{H}_2 + \text{H}_2\text{O}$ collisions, and even transient formation of $\text{H}_2\text{-H}_2\text{O}$ clusters in the cold environment of interstellar clouds.

Beyond issues of van der Waals dimer formation, however, there is also substantial fundamental interest simply in inelastic scattering between H_2 and H_2O species,³⁴ for which the precise intermolecular potential energy surface plays a role of central importance. For example, the lowest rotational spacings in the para H_2 (358 cm^{-1}) and ortho H_2 (600 cm^{-1}) nuclear spin manifolds are greatly in excess³⁵ of those of both para H_2O (37.1 cm^{-1}) and ortho H_2O (18.6 cm^{-1}), where the para/ortho (or p/o) designation refers to $I = 0$ vs $I = 1$ cou-

pling of the H atom nuclear spins. Since H_2 is an extremely poor emitter, collisions between $\text{H}_2 + \text{H}_2\text{O}$ can provide an efficient means for transferring energy into H_2O rotation, which can be radiated away much more efficiently and thereby function as a “coolant” in interstellar clouds.^{36,37} Such a decrease in total energy by radiation can lead to collapse of the cloud, initiating early stages of star formation.³¹ Additionally, $\text{H}_2 + \text{H}_2\text{O}$ collisions are also thought to be responsible for formation of population inversions between H_2O energy levels. This has been invoked³⁸ to explain ubiquitous water maser radiation,³⁹ which has been observed from a variety of extragalactic,⁴⁰ galactic,⁴¹ and interplanetary³¹ objects. The $\text{H}_2\text{-H}_2\text{O}$ dimer potential is also of pivotal interest in formation of H_2 from H atoms. In particular, considerable effort has been put into characterizing $\text{H} + \text{H} \rightarrow \text{H}_2$ reactions catalyzed by solid dust particles,^{42–44} many of which are expected to be quite cold and coated by a water ice mantle.^{25,33} As a result, this requires efficient recombination and desorption⁴⁵ of H_2 from the icy H_2O surface, the detailed $\text{H}_2 + \text{H}_2\text{O}$ interaction potential for which is necessary to characterize these important interstellar rate processes.

In addition to both combustion and interstellar chemistries, the simple $\text{H}_2\text{-H}_2\text{O}$ van der Waals dimer is also of fundamental interest from a purely theoretical perspective. This complex has a small number of electrons ($n = 12$) which greatly facilitates high level *ab initio* efforts. It also contains all but one non-hydrogenic atom, which helps in convergence properties for dynamics calculations in multiple degrees of freedom. As a result this complex offers an unprecedented opportunity for a purely “first principles” test between experiment (i.e., high resolution spectroscopy) and theory (*ab initio*/dynamics calculations). Indeed, the small electron number has already stimulated the development of a high level *ab initio* potential energy surface¹ by Valiron *et al.* in full dimensionality (9D). This has been averaged over H_2 and H_2O intramolecular wavefunctions to provide a vibrationally adiabatic potential in the 5D subspace of intermolecular stretching and internal rotor coordinates, as first obtained by Valiron *et al.* in 2008 for H_2O and H_2 in their vibrational ground states.¹ For the present studies, these calculations have been extended to the vibrationally excited overtone $\nu_{\text{OH}} = 2$ polyad of H_2O , in order to obtain accurate wavefunctions and energy levels relevant for detailed comparison to infrared overtone absorption spectroscopy.

The focus of this paper is twofold. First of all, we present a combination of *ab initio* and multidimensional dynamical calculations to obtain 5D intermolecular wavefunctions and energy levels for complexes of o/p- $\text{H}_2(\nu = 0)$ with both the ground o/p- H_2O [$|00^+\rangle$ or (000)] and overtone excited states of o/p- H_2O [$|02^-\rangle$]. For simplicity, we use the notation by Child, whereby $|02^-\rangle$ refers to the $(\nu_1 \nu_2 \nu_3) = (101)$ combination state with one symmetric and one antisymmetric OH stretch quanta.⁴⁶ These calculations are performed separately for each of the four spin symmetry species (i.e., o H_2 -o H_2O , o H_2 -p H_2O , p H_2 -o H_2O , and p H_2 -p H_2O), which, in conjunction with a simple dipole moment function for $\nu_{\text{OH}} = 2$ excitation, are used to predict first principles infrared overtone absorption spectra for $\text{H}_2\text{-H}_2\text{O}$. As a second thrust of this paper, we describe and present results from a vibrationally mediated

FIG. 1. Multiresonance IR-UV-UV scheme for detecting weakly bound $\text{H}_2\text{-H}_2\text{O}$ clusters. Complexes are formed by (a) collisional cooling in a slit supersonic jet and (b) excited in the $|02^- \rangle$ overtone manifold of the H_2O with an infrared laser pulse. (c) The resulting vibrationally excited H_2O , either after predissociation or while still remaining in the cluster, is photolyzed by a laser at 193 nm to form OH radical. (d) OH photolysis products are detected by laser induced fluorescence following excitation by a tunable 308 nm pulse. Delay between IR and photolysis lasers can be varied to probe predissociation of metastable $\text{H}_2\text{-H}_2\text{O}$ cluster states directly in the time domain.

photodissociation experiment that permits us to quite sensitively observe infrared absorption resonances in $\text{H}_2\text{-H}_2\text{O}$ clusters by selective UV photolysis of vibrationally excited H_2O and laser induced fluorescence detection (LIF) of the resulting OH (Fig. 1). With the aid of the above-mentioned theoretical predictions, we are able to identify and assign rotational progressions due to $\text{oH}_2\text{-oH}_2\text{O}$ clusters in our experimental infrared spectrum. Additionally, both the time delay between infrared and photolysis lasers as well as the OH probe transition can be varied to gain further insight into predissociation dynamics for the complex.

II. THEORETICAL BACKGROUND

A. Potential surfaces

A potential energy surface (PES) for $\text{H}_2\text{-H}_2\text{O}$ that includes all nine internal degrees of freedom has been calculated *ab initio* by Valiron *et al.*^{1,47} with the use of the CCSD(T)-R12 method (coupled-cluster with singles, doubles, and perturbative triples, explicitly correlated). This PES is independent of nuclear mass and can be employed for any of the water-hydrogen isotopologues. Several 5D “rigid-rotor” surfaces have been obtained, either by averaging the 9D potential over vibrational wavefunctions of H_2O and H_2 (or D_2)^{1,17,47} or by fixing the internal geometry of the monomers at vibrationally averaged values, as done for^{18,29,48} $\text{H}_2\text{-HDO}$, $\text{H}_2\text{-D}_2\text{O}$, and $\text{D}_2\text{-D}_2\text{O}$. In the case where both H_2O and H_2 are in their ground vibrational states, Valiron *et al.* have shown that the PES at the average vibrational ground state (VGS) geometry is in very good agreement with the explicitly vibrationally averaged potential (VAP). The corresponding effects on scattering cross sections were examined by Scribano *et al.*,²⁹ with the VGS and VAP potentials shown to provide very similar cross sections even at collision energies below 1 cm^{-1} . The high accuracy of these $\text{H}_2\text{-H}_2\text{O}$ PES’s has also been confirmed recently by a number of comparisons between theory and experiment including inelastic differential cross sections,²⁶ pressure broadening cross sections,^{30,37} elastic integral cross sections,¹⁸ and IR spectra of the complex.^{15,17,21}

In the present work, we use two different vibrationally averaged 5D PES’s, with (i) both H_2 and H_2O monomers in their ground vibrational state (as discussed in Valiron *et al.*¹)

and (ii) ground state $\text{H}_2(v=0)$ and H_2O in its doubly excited $|02^- \rangle$ state, utilizing the wavefunction of Lodi and Tennyson.^{49,50} Both ground and excited state 5D potentials are expressed as a 149 term angular expansion,¹ with coupled spherical harmonics in polar angles for (i) the center of mass vector $\mathbf{R}$ pointing from H_2O to H_2 and (ii) the H_2 axis. These angles are defined with respect to a frame fixed to the H_2O monomer, with the z axis parallel to the C_2 symmetry axis and the xz plane parallel to the plane of the molecule. Note that these are not the same polar angles as the body-fixed (BF) angular coordinates used in the rovibrational level calculations, where the z axis of the BF frame is parallel to the vector $\mathbf{R}$. As shown elsewhere, however, one can analytically transform these angular functions into BF coordinates and directly use the R -dependent coefficients in the expansion of the potential to compute matrix elements of the Hamiltonian.¹⁵ The 149 term angular expansion of the potential is the same as used in Ref. 1. The accuracy of the fit of this expansion to the *ab initio* data points is shown in that reference.

The global minimum corresponds to a planar geometry with C_{2v} symmetry, with a secondary local minimum, non-planar structure (see Figs. 1 and 2 in Ref. 15). The global (local) minimum for *ground state* $\text{H}_2\text{-H}_2\text{O}$ corresponds to a binding energy $D_e = 235.14 \text{ cm}^{-1}$ (199.40 cm^{-1}) and center-of-mass distance R_e of $5.82 a_0$ ($6.07 a_0$), with very small changes for $\text{H}_2\text{-H}_2\text{O}$ with H_2O in its $|02^- \rangle$ excited state ($D_e = 235.66 \text{ cm}^{-1}$, $R_e = 5.81 a_0$ and $D_e = 197.13 \text{ cm}^{-1}$, $R_e = 6.15 a_0$ for the global and local minima, respectively). Both of these geometries may be considered as hydrogen bonded: in the global minimum structure, the H_2 monomer is the donor and H_2O the acceptor, whereas for the local minimum structure, H_2O is the donor and H_2 the acceptor. The $|02^- \rangle \leftarrow |00^+ \rangle$ vibrational excitation needs to be accompanied by a rotational transition in order to make it dipole-allowed. Since this could either be internal (H_2O rotation) or intermolecular (tumbling of the cluster), the observed transitions are sensitive to the anisotropy of the intermolecular potential, and therefore to hindered rotation dynamics of H_2O in the complex.

B. Bound and quasi-bound state calculations

The method to compute the intermolecular rovibrational states on the 5D intermolecular potential surface is based on a general formalism⁵¹ developed for weakly bound dimer molecular complexes with large amplitude internal motion such as ammonia^{52–54} and water^{9,51,55–57} dimer. For details on the Hamiltonian, body-fixed coordinates, etc., the reader is referred to previous work.¹⁵ Rotational constants for H_2O ($A_{\text{gs}} = 27.8806 \text{ cm}^{-1}$, $B_{\text{gs}} = 14.5216 \text{ cm}^{-1}$, and $C_{\text{gs}} = 9.2778 \text{ cm}^{-1}$ for the ground state and $A_{\text{ex}} = 25.95255 \text{ cm}^{-1}$, $B_{\text{ex}} = 14.2100 \text{ cm}^{-1}$, and $C_{\text{ex}} = 8.971415 \text{ cm}^{-1}$ for the $|02^- \rangle$ excited state) and H_2 ($B_0 = 59.3398 \text{ cm}^{-1}$) are taken from experimental values,⁵⁸ with atomic masses of 1.007825 u for H and 15.994915 u for O. A discrete variable representation (DVR) grid in the intermolecular distance contains 96 equidistant points between $R = 4$ and $26 a_0$, contracted as before to form a radial basis of 20 functions.¹⁵ The angular

TABLE I. Symmetry relations in ground state H₂-H₂O: irreducible representations of G_8 , quantum numbers k_A and j_B relevant for symmetry, para/ortho (p/o) nature of the monomers, and nuclear spin statistical weights.

irrep	j_B	H ₂	k_A	H ₂ O	Weight
A ₁ ⁺	Even	p	Even	p	1
A ₁ ⁻	Even	p	Even	p	1
A ₂ ⁺	Even	p	Odd	o	3
A ₂ ⁻	Even	p	Odd	o	3
B ₁ ⁺	Odd	o	Even	p	3
B ₁ ⁻	Odd	o	Even	p	3
B ₂ ⁺	Odd	o	Odd	o	9
B ₂ ⁻	Odd	o	Odd	o	9

basis contains coupled products of symmetric top Wigner D functions⁵⁹ and spherical harmonics for the internal rotations of H₂O and H₂, respectively, multiplied with Wigner D functions for end-over-end rotation of the dimer and truncated at $j_{A\max} = 10$ for H₂O and $j_{B\max} = 8$ for H₂. It was shown in Ref. 15 that the errors in the energy levels caused by the truncation of the basis at these values of j_A and j_B are less than 10^{-5} cm⁻¹.

The permutation-inversion or molecular symmetry group⁶⁰ $G_8 \equiv D_{2h}(M)$ of H₂-H₂O is generated by the permutation operation P_{12} interchanging the H nuclei in H₂O, a similar P_{34} operation that interchanges the H nuclei in H₂, and inversion E^* . Table I lists the resulting nuclear spin weights for the irreducible representations (i.e., irreps) of G_8 , as well as quantum numbers k_A , which determine the para/ortho (p/o) nature of the H₂O states, and j_B , which determines whether the states belong to ortho or para H₂. The quantum number k_A is the projection of the H₂O angular momentum j_A on the C_2 symmetry axis of H₂O. Other (approximate) quantum numbers that are useful to describe and understand the nature of the rovibrational states are m_A and m_B , the projections of the monomer angular momenta j_A and j_B on the dimer axis $\mathbf{R}$, and the projection $K = m_A + m_B$ of the total angular momentum J on this axis. Finally, we observe that the total angular momentum J and the inversion parity $p = \pm 1$ under E^* are exact quantum numbers. In our analysis of the rovibrational states, we use the spectroscopic parity ε , which is related to the inversion parity by $p = \varepsilon (-1)^J$. With this notation, we also follow the convention of using the even/odd spectroscopic parity labels *ef* to distinguish states with $K > 0$.¹⁵ It is worth noting that subscripts A and B always refer to the A and B dimer subunits, rather than, for example, the inertial axes of the H₂O internal rotor. The adaptation of the basis to the irreps of the group G_8 is easy. Basis functions with even/odd values of j_B belong to the A/B irreps, basis functions with even/odd values of k_A belong to the irreps with subscripts 1/2, respectively. The basis is adapted to $\pm$ symmetry under E^* with the use of Eq. (16) in Ref. 15, by taking linear combinations of two primitive basis functions.

The $|02^- \rangle \leftarrow |00^+ \rangle$ excitation energy of H₂O is much larger than the dissociation energy of the complex, but the fast intramolecular vibrations are only weakly coupled to the much slower intermolecular motions, so the excited states of the complex are quasi-bound. As explained in Sec. II A, these

TABLE II. Symmetry relations in H₂-H₂O with H₂O in its excited $|02^- \rangle$ state: irreducible representations of G_8 , intermolecular quantum numbers, and para/ortho (p/o) nature of the monomers.

irrep (total)	irrep (intermolecular)	j_B	H ₂	k_A	H ₂ O
A ₁ ⁺	A ₂ ⁺	Even	p	Odd	p
A ₁ ⁻	A ₂ ⁻	Even	p	Odd	p
A ₂ ⁺	A ₁ ⁺	Even	p	Even	o
A ₂ ⁻	A ₁ ⁻	Even	p	Even	o
B ₁ ⁺	B ₂ ⁺	Odd	o	Odd	p
B ₁ ⁻	B ₂ ⁻	Odd	o	Odd	p
B ₂ ⁺	B ₁ ⁺	Odd	o	Even	o
B ₂ ⁻	B ₁ ⁻	Odd	o	Even	o

excited states are computed as bound levels on the 5D potential surface obtained by averaging the full 9D potential over the $|02^- \rangle$ state vibrational wave function of H₂O and the ground state wave function of H₂, i.e., the vibrational predissociation process is not explicitly considered.

C. Transition selection rules and intensities

The $|02^- \rangle$ vibrational state of H₂O is odd under P_{12} and belongs to the A₂⁺ irrep of the symmetry group G_8 of the complex. The product of the $|02^- \rangle$ wavefunction of the H₂O monomer, the ground state of H₂, and the intermolecular rovibrational wavefunction must obey the usual relations, i.e., pH₂O corresponds to the A₁[±] and B₁[±] irreps, oH₂O corresponds to the A₂[±] and B₂[±] irreps, with A/B corresponding to pH₂/oH₂ and the parity $\pm$ referring to symmetry under inversion E^* . This yields the symmetry relations for the excited state wavefunctions shown in Table II. The local H₂O coordinate frame is chosen with z and x axes along the *inertial* B (i.e., C_2) and A axes, with the molecule lying in the xz plane, by which para(ortho) H₂O wavefunctions can be identified by $k_A = \text{even(odd)}$. The only nonzero component of the $|02^- \rangle \leftarrow |00^+ \rangle$ transition dipole moment is the A-type component μ_x , which is invariant under all permutations, odd under inversion, and therefore has symmetry A₁⁻. If we take the matrix element of μ_x between the ground state intramolecular wavefunction of A₁⁺ symmetry and the $|02^- \rangle$ excited state wavefunction of A₂⁺ symmetry, the resulting $|02^- \rangle \leftarrow |00^+ \rangle$ transition dipole moment function depends only on the intermolecular coordinates and has symmetry A₂⁻. This leads to the selection rules for the intermolecular vibrational states given in Table III, with a detailed derivation of the correct line strengths clarified in the Appendix.

III. CALCULATED RESULTS

All bound rovibrational levels on the ground state intermolecular potential and all quasi-bound levels on the excited state potential have been calculated as a function of total angular momentum J and all four ortho/para combinations of H₂ and H₂O. The ground state levels for all four nuclear spin species have been reported previously in Ref. 15 with the four sets of levels for the excited state potential listed in

TABLE III. Selection rules for the intermolecular rovibrational states involved in dipole transitions in $\text{H}_2\text{-H}_2\text{O}$ accompanying the $|02^- \rangle \leftarrow |00^+ \rangle$ transition in the H_2O monomer.

Ground state irrep		$ 02^- \rangle$ state irrep (intermolecular)	H_2	H_2O
A_1^+	$\rightarrow$	A_2^-	p	p
A_1^-	$\rightarrow$	A_2^+	p	p
A_2^+	$\rightarrow$	A_1^-	p	o
A_2^-	$\rightarrow$	A_1^+	p	o
B_1^+	$\rightarrow$	B_2^-	o	p
B_1^-	$\rightarrow$	B_2^+	o	p
B_2^+	$\rightarrow$	B_1^-	o	o
B_2^-	$\rightarrow$	B_1^+	o	o

Tables IV–VII. Information on the ground state Σ , Π , or Δ character (with approximate quantum numbers $K = 0, 1$, or 2) can also be found in Ref. 15. It is shown there that the lowest state is of Σ character ($K = 0$) for all dimer species except for the $\text{oH}_2\text{-oH}_2\text{O}$ dimer, where the lowest state has Π character ($K = 1$). One potential source of confusion between ground state and the vibrationally excited $|02^- \rangle$ state levels concerns the assignment to oH_2O vs. pH_2O species, which arises due to antisymmetry with respect to exchange of identical fermionic H atoms. Specifically, the H_2O $|02^- \rangle$ vibrational wavefunctions are already antisymmetric with respect to such exchange; as a result, the internal rotor rovibrational levels associated with the excited vs. ground state potential surface of the complex have o and p labels interchanged. It is also worth noting that levels on the excited state potential are more strongly bound (by 2–3 cm^{-1}) than those of the same symmetry on the ground state potential, despite only minor changes in the intermolecular surfaces. This is predominantly because the H_2O rotational constants *decrease* in the excited $|02^- \rangle$ state, and thus the zero-point energy associated with the hindered internal rotations is lowered correspondingly.

TABLE IV. Rovibrational levels of symmetry $A_2^\pm$ of $\text{pH}_2\text{-pH}_2\text{O}$ $|02^- \rangle$ (in cm^{-1}). The dissociation limit to form pH_2 ($j = 0$) and pH_2O $|02^- \rangle$ 1_{01} is at 23.7994 cm^{-1} ; thus the dissociation energy $D_0 = 38.07 \text{ cm}^{-1}$. In parentheses is the Σ or Π character, which is higher than 99% if not otherwise indicated. The parity e/f is the spectroscopic parity.

$\Sigma(K = 0)$				
Parity	$J = 0$	$J = 1$	$J = 2$	$J = 3$
e	– 14.2720	– 13.5226 (90%)	– 11.7442 (80%)	– 8.7553 (73%)
e	20.9514	20.9433 (64%)	21.6149 (57%)	22.8614 (53%)
f	12.3387	14.0284 (96%)	17.3196 (91%)	22.0751 (85%)
$\Pi(K = 1)$				
Parity	$J = 1$	$J = 2$	$J = 3$	
e	– 7.1213 (90%)	– 3.4031 (80%)	1.7787 (73%)	
e	4.2473	7.0008	11.1029	
e	22.7788 (65%)			
f	– 7.7672	– 5.0476	– 1.0071	
f	3.8823 (96%)	5.9760 (91%)	9.2156 (86%)	
f	22.1423	23.2544		

TABLE V. Rovibrational levels of symmetry $A_1^\pm$ of $\text{pH}_2\text{-oH}_2\text{O}$ $|02^- \rangle$ (in cm^{-1}). The dissociation limit to form pH_2 ($J = 0$) and oH_2O $|02^- \rangle$ 0_{00} is defined to be at 0.00 cm^{-1} energy; thus the dissociation energy is $D_0 = 34.53 \text{ cm}^{-1}$.

$\Sigma(K = 0)$				
Parity	$J = 0$	$J = 1$	$J = 2$	$J = 3$
e	– 34.5328	– 33.1532	– 30.4075	– 26.3243
e	– 2.9507	– 2.2637 (95%)	– 0.8188 (94%)	

The wavefunctions and formulae in the Appendix permit us to calculate line strengths for all allowed $\Delta J = 0$ and ± 1 transitions between all bound levels with $J = 0\text{--}6$ on the ground and excited state potentials (complete results available in the supplementary material⁷⁶). Transitions with $\Delta J = \pm 1$ occur between ground and excited state levels of the same spectroscopic parity: $e \rightarrow e$ and $f \rightarrow f$, while transitions with $\Delta J = 0$ require a change of spectroscopic parity: $e \rightarrow f$ and $f \rightarrow e$. The calculated line strengths and the Boltzmann factors for the ground state levels combine to yield detailed spectral simulations for each of the four ortho/para combinations of

TABLE VI. Rovibrational levels of symmetry $B_2^\pm$ of $\text{oH}_2\text{-pH}_2\text{O}$ $|02^- \rangle$ (in cm^{-1}). The dissociation limit to form oH_2 ($j = 1$) and pH_2O $|02^- \rangle$ 1_{01} is at 142.4790 cm^{-1} ; thus the dissociation energy $D_0 = 62.07 \text{ cm}^{-1}$.

$\Sigma(K = 0)$				
Parity	$J = 0$	$J = 1$	$J = 2$	$J = 3$
e	90.7607	92.3868 (98%)	95.5992 (95%)	100.3258 (91%)
e	112.8261	113.9473 (97%)	116.2190 (93%)	119.6747 (89%)
e	135.8546	136.9280 (95%)	138.8707 (90%)	141.5769 (65%)
e	139.7633	140.9057 (94%)		
f	96.2396	97.0102 (74%)	99.0267 (63%)	102.3673 (57%)
f	118.9932	120.3044 (97%)	122.9131 (90%)	126.8016 (79%)
f	126.7211	127.9918	130.5230 (97%)	134.2767 (94%)
f	139.8353	140.7114 (91%)	142.3644 (73%)	
$\Pi(K = 1)$				
Parity	$J = 1$	$J = 2$	$J = 3$	
e	80.4069 (98%)	82.8192 (95%)	86.4685 (91%)	
e	98.6498	101.1751 (97%)	104.9825 (94%)	
e	123.0357 (97%)	126.2302 (86%)	130.7134 (77%)	
e	132.9728 (94%)	134.2682 (85%)	136.4236 (78%)	
e	138.0829 (97%)	139.3161 (87%)	141.1240 (57%)	
f	80.6253	83.4491 (99%)	87.6636 (98%)	
f	99.2279 (74%)	102.3898 (62%)	106.7318 (53%)	
f	122.8846 (97%)	125.8496 (84%)	130.1521 (73%)	
f	133.306	135.113 (98%)	137.7444 (94%)	
f	137.9746 (92%)	138.9842 (78%)	140.6585 (71%)	
$\Delta(K = 2)$				
Parity	$J = 2$	$J = 3$		
e	109.2813 (98%)	113.3813 (95%)		
e	123.8142 (92%)	127.7350 (86%)		
e	141.3118 (86%)			
f	109.3114 (97%)	113.5212 (92%)		
f	123.8082 (89%)	127.7344 (77%)		
f	141.2413 (83%)			

TABLE VII. Rovibrational levels of symmetry $B_1^\pm$ of $\text{oH}_2\text{-oH}_2\text{O } |02^- \rangle$ (in cm^{-1}). The dissociation limit to form oH_2 ($j = 1$) and $\text{oH}_2\text{O } |02^- \rangle 0_{00}$ is at 118.6796 cm^{-1} ; thus the dissociation energy $D_0 = 56.26 \text{ cm}^{-1}$.

$\Sigma(K = 0)$				
Parity	$J = 0$	$J = 1$	$J = 2$	$J = 3$
e	62.4181	63.8496	66.7038 (99%)	70.9616 (98%)
e	107.7671	108.9822 (92%)	111.2160 (83%)	114.0028 (53%)
e	113.1361	114.2694 (98%)	116.6432 (86%)	
f	115.0996	116.3106 (81%)		
$\Pi(K = 1)$				
Parity	$J = 1$	$J = 2$	$J = 3$	
e	79.3032	81.9811 (99%)	85.9748 (98%)	
e	107.9309 (92%)	110.3614 (81%)	114.1719 (50%)	
e	117.3353 (98%)			
f	79.3623	82.1564	86.3196	
f	107.9024 (98%)	110.2522 (94%)	113.7747 (90%)	
f	117.4753 (84%)	118.1563 (73%)		
$\Delta(K = 2)$				
Parity		$J = 2$	$J = 3$	
e		116.0461 (91%)		
f		116.0750 (95%)		

$\text{H}_2\text{-H}_2\text{O}$, which are then used to assign and interpret the experimentally measured action spectra (*vide infra*).

IV. EXPERIMENTAL

The experimental apparatus for obtaining the $\text{H}_2\text{-H}_2\text{O}$ cluster overtone spectra has been described previously,^{12,61} therefore, only a brief overview and details relevant to these specific studies will be necessary. Water-hydrogen gas mixtures are prepared by bubbling pure (99.99%) H_2 through a sealed reservoir filled with purified ($\rho = 10 \text{ M}\Omega\cdot\text{cm}$) and degassed water. The stainless steel reservoir is held at 0°C by immersing in an ice water bath in order to maintain a steady water vapor pressure⁶² of 4.6 Torr. In addition, this “precooling” ensures that all downstream components of the gas delivery system are at a higher temperature than the liquid reservoir, thus ensuring no condensation once the mixture has been formed. Water partial pressure is fixed by maintaining a constant H_2 gas pressure in the bubbler, with the pulsed jet stagnation pressure independently controlled by a needle valve immediately downstream. Total pressure inside the bubbler is monitored with a Baratron capacitance manometer and used to infer $\text{H}_2/\text{H}_2\text{O}$ molar ratios. Typical values of 0.1% water are found to optimize $\text{H}_2\text{-H}_2\text{O}$ cluster formation, presumably because richer mixtures reduce dimer population in favor of larger complexes. A second Baratron monitors and stabilizes pressure in the jet source stagnation region at 550 Torr to yield maximal OH signal production for $\text{H}_2\text{-H}_2\text{O}$.

The $\text{H}_2/\text{H}_2\text{O}$ mixture is delivered to a home built slit jet source described extensively in Ref. 63. A 1 ms pulse duration and 100 ms spacing between valve firing events results in a 99% reduction in average versus peak gas flow, allowing the chamber to be maintained at $\sim 10^{-5}$ Torr with a 4500 L/s

FIG. 2. Action spectrum obtained by LIF detection of OH ($^2\Pi_{3/2}^e$, $N = 8$) while tuning infrared excitation frequency at a fixed IR-photolysis time delay of 30 ns. The spectrum is dominated by water monomer transitions from the lowest (o/p) H_2O rotational energy states in each nuclear spin manifold (1_{01} ortho and 0_{00} para). Blow ups (see above) reveal two bands of smaller peaks due to $\text{H}_2\text{-H}_2\text{O}$ clusters in the supersonically cooled beam, one near the free oH_2O transition $|02^- \rangle 0_{00} \leftarrow |00^+ \rangle 1_{01}$, with the other near the IR forbidden “Q-branch” $|02^- \rangle$ vibrational band origin of the oH_2O monomer.

diffusion pump backed by a 25 L/s mechanical pump. Action spectra of water monomer species that remain unclustered in the beam (Fig. 2) show no rotational excitation above the signal to noise level. This yields an upper limit of $T_{\text{rot}} < 5.1 \text{ K}$ for the jet temperature, which compares favorably with $T_{\text{rot}} \approx 3.5 \text{ K}$ temperatures predicted from modeling⁶⁴ the slit jet as an isentropic expansion. As a result, H_2O cools exclusively down into the two lowest nuclear spin states, which do not interconvert on the expansion time scale. Due to the requirement of exchange symmetry for the two identical hydrogen atoms, the ortho and para populations conform to the expected nuclear spin ratio of 3:1 for $J_{\text{KaKc}} = 1_{01}$ and 0_{00} states, respectively. While not observed directly, a similar 3:1 ratio is anticipated for ortho ($J = 1$) and para ($J = 0$) H_2 in the supersonic expansion.

The three laser cluster detection scheme is summarized in Fig. 1. Vibrational excitation of H_2O , either in the $\text{H}_2\text{-H}_2\text{O}$ cluster or after predissociation, is achieved with an optical parametric oscillator (OPO) laser pumped by 532 nm light. The idler beam is extracted from the OPO cavity and directly sent into the vacuum chamber with 3 mJ/pulse energies and 0.2 cm^2 spot size area. At these intensities, H_2O in the 1_{01} rotational state has only a 5% probability⁶⁵ of absorbing an IR photon, resulting in a safely negligible ($< 3 \times 10^{-3}$) probability for multiple photon absorption. In order to probe the expected range of $\text{H}_2\text{-H}_2\text{O}$ absorptions, the laser frequency is tuned from 7210 cm^{-1} to 7310 cm^{-1} , with a small IR pickoff sent through an optoacoustic cell filled with 5 Torr of H_2O . A typical Doppler broadened H_2O line in such a cell ($\Delta\nu \approx 0.02 \text{ cm}^{-1}$) is > 10 -fold narrower than the OPO laser ($\Delta\nu \approx 0.25 \text{ cm}^{-1}$), and thus provides a convenient frequency axis calibration by linear interpolation between known frequencies

in the sufficiently dense (~ 2 lines/ cm^{-1}) room temperature water absorption spectrum.⁶⁵

A digital delay generator provides a variable waiting time between the OPO and 193 nm excimer laser and therefore probes predissociation dynamics on time scales ranging from ~ 5 ns to $1 \mu\text{s}$. The 193 nm UV beam (15 mJ/pulse, $\sim 0.5 \text{ cm}^2$ area) selectively photolyzes the vibrationally excited H_2O to make OH radicals, which are subsequently detected by a third LIF laser (303–310 nm, beam energy ~ 2.5 mJ), obtained from frequency doubling the output of a dye laser pumped by a frequency doubled YAG laser. All three beams enter/exit the chamber through CaF windows tilted at Brewster's angle in order to minimize reflections of the p-polarized probe radiation which can lead to appreciable background. Furthermore, the 2 mm LIF probe beam travels through 8 annular optical baffles with inner diameter of 1 cm to further minimize the amount of window scatter entering the chamber.

Fluorescence emission from electronically excited OH is collected by a fused silica lens ($f = 5$ cm) positioned 5 cm from the excitation region, before passing through a fused silica chamber window and a Schott UG11 filter to block scatter from the 193 nm photolysis pulse. The LIF photons are imaged onto a solar blind 14 stage photomultiplier tube (PMT) with a gain at 1700 V of $\sim 5 \times 10^6$ electrons/photon, sending the subsequent electrical current through a 50Ω load resistor, across which a voltage is amplified ($\times 20$), collected by boxcar integration between 10 ns and $1 \mu\text{s}$ after the probe beam, thereby capturing the majority of fluorescence photons over the $\sim 1 \mu\text{s}$ lifetime of the electronically excited OH molecules. The PMT voltage is then averaged over the boxcar detection window before being sent through an A/D converter and then recorded using a Labview program which also controls scanning of the IR excitation laser or the UV probe beam. The energy is monitored in real time with a diode power

meter, with the final LIF signal scaled to eliminate pulse-to-pulse variation in the probe laser beam.

V. RESULTS

A. Experimental spectra and *ab initio* predictions

As immediately evident in Fig. 2, the action spectrum obtained by scanning the infrared excitation laser is completely dominated by overtone $|02^- \rangle \leftarrow |00^+ \rangle$ transitions (i.e., $(101) \leftarrow (000)$ in normal mode notation) of the H_2O monomer, which attests to the limited degree of clustering occurring in the predominantly H_2 supersonic jet. However, upon closer inspection, a closely spaced progression of smaller peaks are observed with intensity above the signal to noise limit, as shown in the blowups in Fig. 2. These transitions do not correspond to any nearby peaks from water monomer bands such as the $|02^+ \rangle \leftarrow |00^+ \rangle$ overtone symmetric stretch excitation (i.e., $(200) \leftarrow (000)$ in normal mode notation), nor can they be assigned to overtone transitions in any H/D isotopomers of H_2O . Since H_2 monomers do not exhibit any absorption due to lack of an infrared transition dipole moment, the small peaks in Fig. 2 almost certainly reflect $\text{H}_2\text{-H}_2\text{O}$ clusters in the jet.

The *ab initio*/vibrational dynamics calculations described in the first half of this paper play a critical role in confirming such an assignment. We start by building intuition with BF eigenfunctions generated from the 5D $\text{H}_2\text{-H}_2\text{O}$ potential surface for the excited $|02^- \rangle$ H_2O vibrational state. Specifically, Fig. 3 displays 2D slices through these eigenfunctions in the polar angles $\beta_{\text{H}_2\text{O}}$ and β_{H_2} , for the lower Σ (left panel) and first excited Π (right panel) internal rotor states of the $\text{oH}_2\text{-oH}_2\text{O}$ complex. Note that both states are built from the nominally “non-rotating” $j_{ka}k_c = 0_{00}$ internal rotor oH_2O state, so

FIG. 3. Planar cuts through the total $J = 1$ wave functions for (a) the $\Sigma(1,0_{00})$ ground state and (b) the $\Pi(1,0_{00})$ state of $\text{oH}_2\text{-oH}_2\text{O } |02^- \rangle$. $\beta_{\text{H}_2\text{O}}$ and β_{H_2} represent polar angles of the H_2O symmetry axis and the H_2 bond axis in the body-fixed (BF) dimer frame. The global minimum with H_2O as the acceptor corresponds to $\beta_{\text{H}_2\text{O}} = 0^\circ$ and $\beta_{\text{H}_2} = 0^\circ$ or 180° . The local minimum, where H_2O behaves as a hydrogen bond donor, occurs at a non-planar structure which projects onto $\beta_{\text{H}_2\text{O}} = 119^\circ$ and $\beta_{\text{H}_2} = 90^\circ$. The dotted lines correspond to the range of planar geometries where the OH stretch aligns with the intermolecular axis. These geometries are expected to most efficiently couple $|02^- \rangle$ H_2O vibrational motion into the dissociation coordinate and are sampled much more extensively in the $\Pi(1,0_{00})$ vs. $\Sigma(1,0_{00})$ states.

that the Σ vs Π projection comes predominantly from angular momentum $j = 1$ of the oH_2 subunit. In general, both wavefunctions are characterized by large amplitude quantum motion and significant departure from the global minimum energy “hydrogen bond acceptor” structure for H_2O at $\beta_{\text{H}_2\text{O}} = 0^\circ$ and $\beta_{\text{H}_2} = 0^\circ, 180^\circ$, even partially sampling the higher minimum energy “hydrogen bond donor” structure at $\beta_{\text{H}_2\text{O}} = 128^\circ$ and $\beta_{\text{H}_2} = 90^\circ$. This confirms the zeroth order nature of H_2 and H_2O wavefunctions in the complex as that of nearly free internal rotors, with angular motion weakly coupled by the anisotropy in the potential energy surface. Thus, a more complete description of the states in Fig. 3(a) for $\text{oH}_2\text{-oH}_2\text{O}$ would be $\Sigma(1,0_{00})$ and $\Pi(1,0_{00})$, where the first and second terms in parentheses refer to the corresponding free monomer descriptions of H_2 and H_2O angular momenta, respectively.

Based on calculated energies and wavefunctions for all levels in both ground and internally vibrationally excited $|02^-)$ states and the transition line strengths, it is possible to predict an infrared spectrum of the complex from first principles. A small sample segment of this is shown in Fig. 4(a), where observed lines are labeled using symmetric top notation as $^{\Delta K}\Delta J_{K''}(J'')$. A 3.8(3) K beam temperature best fits the data, i.e., cold but nevertheless achievable in the slit supersonic expansion and in agreement with the previously determined upper limit of 5 K. Despite potential complications associated with action spectroscopy vs direct absorption spectroscopy based intensities, the degree of agreement observed between experiment and theory is extremely encouraging. In particular, this provides strong evidence for assignment of the peaks in the $0_{00} \leftarrow 1_{01}$ monomer region as coming from the corresponding $\Sigma(1,0_{00}) \leftarrow \Pi(1,1_{01})$ free internal rotor transition in the $\text{oH}_2\text{-oH}_2\text{O}$ complex, blueshifted by $\approx 4\text{ cm}^{-1}$ from the $0_{00} \leftarrow 1_{01}$ transition of the H_2O moiety at 7226 cm^{-1} due to presence of the $\text{H}_2(j=1)$.

In addition, a weaker second set of transitions is observed near the water monomer band origin^{35,66} at $\nu_0 = 7249.823\text{ cm}^{-1}$ (Fig. 4(b)), where again experiment and theory agree reasonably well on the various infrared transitions, providing further support for assignment to the $\text{oH}_2\text{-oH}_2\text{O}$ dimer species. Interestingly, there are no allowed transitions for H_2O monomer in the band origin region, with appearance of spectral structure only made possible by angular anisotropy in the potential. Simply stated, the potential anisotropy makes j an imperfect quantum number for the H_2O subunit, and therefore generates oscillator strength on the nominally “forbidden” Q-branch transitions corresponding to zero change in monomer angular momentum. The presence of comparably strong P,Q,R-branch features for the cluster and the expected cold temperature of the supersonic jet identify this as a progression in the $\Pi(1,0_{00}) \leftarrow \Pi(1,1_{01})$ band, which probes a second, completely independent internal rotor state in the $|02^-)$ manifold. Note that our $\Pi(1,0_{00})$ labelling of in the upper state implies that the net angular momentum projection ($K=1$) now arises predominantly from the oH_2 rather than the oH_2O subunit. As will be discussed in more detail in Sec. V B, this provides access to photolysis and predissociation dynamics in two quite different metastable upper states of the $\text{oH}_2\text{-oH}_2\text{O}$ cluster.

FIG. 4. Sample comparison between first principles *ab initio*/dynamical theory calculations (colored lines, downward) and experimental spectra (black lines, upward). Excellent agreement between experiment and theory ($T_{\text{rot}} \approx 3.8(3)\text{ K}$) allows assignment of the observed structure to (a) $\Sigma(1,0_{00}) \leftarrow \Pi(1,1_{01})$ and (b) $\Pi(1,0_{00}) \leftarrow \Pi(1,1_{01})$ internal rotor bands of $\text{oH}_2\text{-oH}_2\text{O}$ (red). (c) In contrast, the $\text{oH}_2\text{-pH}_2\text{O}$ species (yellow) reveal no peaks near the predictions, despite the fact that such transitions would be well above the signal to noise for a 3:1 ortho/para nuclear spin ratio. Lines are labeled in symmetric top notation according to $^{\Delta K}\Delta J_{K''}(J'')$.

Finally, we see no evidence within our signal to noise limits for experimental action spectra corresponding to $\text{oH}_2\text{-pH}_2\text{O}$ complexes. The relevant scan region is shown in Fig. 4(c), which displays sample *ab initio*/dynamics predictions for the $\Pi(1,1_{01}) \leftarrow \Sigma(1,0_{00})$ and $\Sigma(1,1_{01}) \leftarrow \Sigma(1,0_{00})$ bands of $\text{oH}_2\text{-pH}_2\text{O}$. Note that these band origins lie 9 cm^{-1} to the red and a few cm^{-1} to the blue, respectively, of the associated $1_{01} \leftarrow 0_{00}$ transition at 7273 cm^{-1} for the free pH_2O monomer. It is important to consider that these intensity

predictions are based on incorporation of ortho/para H_2O nuclear spin states into the complexes in a 3:1 ratio, which may be influenced by “chaperone” displacement effects in the slit jet expansion. As we shall see later, a more intriguing dynamical possibility is that the predissociation rates out of both $\Pi(1,1_{01})$ and $\Sigma(1,1_{01})$ upper states of $\text{oH}_2\text{-pH}_2\text{O}$ are sufficiently high for lifetime broadening to exceed the 0.5 cm^{-1} IR laser line width, and thereby greatly decrease the spectral signal to noise.

B. Vibrational predissociation dynamics

We can take these studies considerably further by exploring (i) the product state distributions of the nascent OH photofragment as well as (ii) the predissociation time scale on which these distributions evolve. By way of example, Fig. 5 displays the nascent rotational state distribution in the $^2\Pi_{1/2}^f(N)$ OH manifold, subsequent to $^{\text{P}}\text{P}_1(1)$ infrared excitation of $\text{oH}_2\text{-oH}_2\text{O}$ clusters in the $\Sigma(1,0_{00}) \leftarrow \Pi(1,1_{01})$ band and for an IR-photolysis delay of 30 ns. Interestingly, the rotational distribution is *quite hot*, peaking at an OH tumbling angular momentum of $N = 6$. This is in sharp contrast with the extremely *cold* rotational distributions observed in the absence of the H_2 via overtone vibrationally mediated photolysis studies of the oH_2O monomer out of the $|02^- \rangle 0_{00}$ rotational state. Interestingly, however, this rotationally hot distribution from $\text{oH}_2\text{-oH}_2\text{O}$ dimer is nearly identical to vibrationally mediated photolysis results¹² obtained for $\text{Ar-oH}_2\text{O}$ and $\text{H}_2\text{O-H}_2\text{O}$. Clearly the presence of even weakly bound species such as H_2 can be responsible for qualitative changes in the resulting energy flow and photolysis dynamics of the excited H_2O subunit.

This point deserves further discussion. First of all, though $\text{OH}(N = 6)$ corresponds to $\approx 850\text{ cm}^{-1}$ rotational energy, this is actually rather modest ($<5\%$) compared to the $\approx 17\,860\text{ cm}^{-1}$ available after overtone IR excitation ($\approx +7229\text{ cm}^{-1}$), cluster dissociation ($\approx -56\text{ cm}^{-1}$),

193 nm photolysis ($\approx +51\,813\text{ cm}^{-1}$) and H-OH bond breaking ($\approx -41\,128\text{ cm}^{-1}$) events. Secondly, as discussed in more detail below, these scans are performed at long IR-photolysis time delay compared to the predissociation lifetime of the complex, which means that photolysis is of the free H_2O monomer rather than an intact $\text{H}_2\text{-H}_2\text{O}$ cluster. Thirdly, photojection of a light H atom species from rovibrationally cold H_2O on the A state surface is known to generate low rotational excitation in the resulting OH fragment. Therefore, the remarkable similarity of product OH distributions obtained from overtone vibrationally mediated photolysis of $\text{M-H}_2\text{O}$ clusters for $\text{M} = \text{Ar}, \text{H}_2\text{O}$, and H_2 is more likely an indication of qualitatively similar rovibrational excitation levels *remaining* in the H_2O molecule *after* the predissociation event. Specifically, $\text{Ar-H}_2\text{O}$ predissociation from the $|02^- \rangle$ overtone state has previously been predicted to occur via near resonant energy transfer of one asymmetric stretch vibrational quantum into two quanta of the H-O-H bending mode. This would indeed be consistent with Fig. 5, as excitation in the HOH bending coordinate is predicted from a Franck-Condon perspective to correlate with the much hotter OH rotation distributions observed. Finally, it is interesting to note that the OH rotational distributions observed from vibrational overtone mediated photolysis of each cluster species vary *smoothly* with N . This is in dramatic contrast with the high contrast, quantum interference oscillations in population vs. N for photolysis of $|02^- \rangle \text{H}_2\text{O}$ from its lowest rotational state(s). As a simple physical picture, this might suggest either disruption of the quantum phase relationships between the outgoing H and OH fragments in the presence of a third body (i.e., H_2 , Ar, or H_2O), or simply a blurring of this interference structure due to rotational excitation of the bare H_2O monomer by predissociation prior to the photolysis event.

We can take this one step further by studies of predissociation dynamics in the time domain. As shown in Fig. 6, the

FIG. 5. OH ($^2\Pi_{1/2}^f$) rotational distributions for the IR laser fixed on the $^{\text{P}}\text{P}_1(1)$ [$\Sigma \leftarrow \Pi$] transition of $\text{oH}_2\text{-oH}_2\text{O}$. The rotationally hot distribution ($N \approx 6$) is due to 193 nm photolysis out of bend excited H_2O states formed by cluster predissociation.

FIG. 6. Direct measurement of $\text{oH}_2\text{-oH}_2\text{O}$ ($|02^- \rangle, \Sigma(1,0_{00})$) predissociation lifetime, obtained by varying the time delay between the infrared and photolysis laser pulses for a specific cluster transition and OH level. The measured lifetime of $15(2)\text{ ns}$ is large compared to the instrument response function of $8.0(3)\text{ ns}$, as determined by observing OH from vibrationally mediated photolysis of H_2O monomer (see inset).

observed OH ($N = 8$) population exhibits a slow sigmoidal increase with time delay between infrared [$|02^- \rangle$ $^3P_1(1)$] cluster excitation and photolysis (193 nm) pulses. Since the photolysis process is essentially prompt, this provides an opportunity to make direct measurement of the predissociation timescale of the initial metastable cluster. Indeed, the inset in Fig. 6 shows the result of such a time delay scan for the corresponding H_2O monomer line. This yields an instrument response function (IRF) of 8.0(3) ns, which is entirely dominated by finite duration of pump and photolysis laser beams, but significantly faster than experimental rise times observed for the cluster. For the $|02^- \rangle$ $\Sigma(1,0_{00})$ $J = 0$ upper state of oH_2-oH_2O accessed by $|02^- \rangle$ $^3P_1(1)$ excitation at ≈ 7228.5 cm^{-1} , least squares deconvolution of signal and IRF yields a predissociation lifetime of 15(2) ns, i.e., in roughly twofold excess of the detection limit. These lifetimes might also be anticipated to depend sensitively on intermolecular orientation of the H_2 and H_2O subunits. Indeed, by way of contrast, similar study of excitation to the corresponding $|02^- \rangle$ $\Pi(1,0_{00})$ state yields a predissociation lifetime of $<5(2)$ ns, i.e., indistinguishable from the IRF. Additional support for such a dynamical trend can be rationalized by inspection of the corresponding intermolecular wavefunctions for these excited states, as will be explored below.

VI. DISCUSSION

As one major goal of this work, we take the opportunity for a detailed comparison between quantum state resolved experimental spectra and first principles *ab initio* and dynamical theory. Indeed, consensus between experiment and theory is quite remarkable (see Fig. 4), with a sub- cm^{-1} level of agreement already 3 orders of magnitude smaller than the ≈ 235 cm^{-1} equilibrium 5D well depths for the $(o/p)H_2-(o/p)H_2O$ potential surfaces. However, closer inspection of the least squares fits reveals that theoretical peak positions are slightly but systematically *blue shifted* ($+0.195(7)$ cm^{-1}) relative to the experimental value. Note that our 5D theoretical framework does not allow intramolecular relaxation of either O-H or H-H bonds due to the presence of the other species in the cluster. Nevertheless, the global 9D minimum would be expected to reveal weak stretching of these coordinates due to hydrogen H atom and water oxygen attraction. This leads to a slight reduction in the oxygen atom confinement, resulting in lower energies for both ground $|00^+ \rangle$ and excited $|02^- \rangle$ levels of the H_2O moiety. However, due to enhanced anharmonic sampling of the potential, one expects additional relaxation in the vibrationally excited state upper state, thus rationalizing a small but systematic ≈ 0.2 cm^{-1} blue shift between reduced dimensionality theory and “full D” experimental data.

A more fundamentally challenging issue arises when one considers the notable absence of any nuclear spin species other than oH_2-oH_2O in the observed spectrum. Due to the long spin flip thermalization time scales for this degree of freedom, the relative abundances of both $[oH_2]/[pH_2]$ and $[oH_2O]/[pH_2O]$ are expected to be very close to their spin-degeneracy ratios (3:1), as is indeed seen in the room temperature stagnation region of the pulsed jet source. Therefore, purely statistical arguments would predict relative 9:3:3:1

TABLE VIII. Ground vibrational state $|00^+ \rangle$ dissociation energies (D_0) for each of the four $(o/p)H_2-(o/p)H_2O$ nuclear spin symmetries with respect to the lowest asymptotic rotor states for the correct nuclear spin modification. Note that these values are somewhat greater ($\approx 2-9$ cm^{-1}) than reported in the present work for the $|02^- \rangle$ vibrational upper states, due to slight differences in the adiabatically averaged full D potentials.

Species	Binding energy (cm^{-1})
oH_2-oH_2O	59.04
oH_2-pH_2O	53.60
pH_2-oH_2O	36.63
pH_2-pH_2O	33.57

abundances for $(oH_2-oH_2O):(oH_2-pH_2O):(pH_2-oH_2O):(pH_2-pH_2O)$, respectively. Fig. 4(c) shows sample results of such predictions for nuclear spin abundances fixed to the above ratios, with rotational distributions separately thermalized at 3.8 K. This dataset makes immediately clear that statistical ratios of both oH_2-pH_2O and pH_2-pH_2O would lead to populations well above the signal to noise limit and yet not observable in the experimental spectrum.

A partial explanation can be found in the “chaparone effect,” which is a consequence of the different ground state binding energies of the various species (Table VIII) and the 1000:1 abundance of H_2 vs. H_2O in the jet. In this model, pH_2-oH_2O and pH_2-pH_2O form early in the supersonic jet, with subsequent collisions with oH_2 displacing the more weakly bound pH_2 and systematically depleting the pH_2 vs oH_2 containing clusters. The reverse process, $pH_2 + oH_2-H_2O \rightarrow pH_2-H_2O + oH_2$, is suppressed by a $\Delta D_0 \approx 20$ cm^{-1} difference in binding energy for ortho vs. para H_2 , which, by detailed balance arguments, plays a dramatic role at low jet temperatures. In the high collision regime, the number of pH_2 vs. oH_2 clusters at thermal equilibrium would be disfavored by a factor of $e^{-20/2.7} = 6 \times 10^{-4}$, i.e., sufficient to diminish signals below the detection limit. Precedent for such differential binding affinities of ortho vs para H_2/D_2 has already been well established in previous high resolution IR studies of $(o/p)H_2-HF$ and $(o/p)D_2-HF$.^{67,68} Indeed, the most convincing comparison can be made with spectroscopic studies on exactly the same $(o/p)H_2-(o/p)H_2O$ clusters in the fundamental HOH bend region, for which both pH_2-pH_2O and pH_2-oH_2O remained unobserved despite even higher signal to noise ($>20:1$) on the corresponding oH_2-pH_2O and oH_2-oH_2O nuclear spin species.²⁰

However, this does not explain the absence of oH_2-pH_2O vs. oH_2-oH_2O clusters (see Fig. 4(c)), for which a differential binding energy of $\Delta D_0 \approx 5.5$ cm^{-1} would only predict a four- to fivefold reduction in equilibrium population even under supersonic jet conditions. More importantly, the fractional concentrations of both oH_2O vs. pH_2O reagent are very minor components ($<0.1\%$) in the supersonic jet, resulting in vanishingly low collision rates for such processes to reach local thermal equilibrium. Indeed, the previous spectroscopic studies in the bend region noted above yielded high quality spectra of both oH_2-oH_2O and oH_2-pH_2O clusters in the anticipated $\approx 3:1$ ratio.²⁰ Clearly some other phenomenon unique to $|02^- \rangle$

excitation must be invoked to explain the *non-observance* of the $\text{oH}_2\text{-pH}_2\text{O}$ species in the present studies.

Though this will require further experimental and theoretical efforts, one possibility worth exploring is rapid predissociation of $\text{oH}_2\text{-pH}_2\text{O}$ ($|02^- \rangle$), which could broaden the IR transitions sufficiently to make them unobservable. Such broadening has in fact been observed²⁰ in our group via high resolution laser absorption for $\text{oH}_2\text{-pH}_2\text{O}$ and $\text{oH}_2\text{-oH}_2\text{O}$ clusters in the HOH bend fundamental region. However, while these previous measurements reported predissociation lifetimes of 5.1(1) ns, 1000-fold faster values would be required to achieve $\sim 1 \text{ cm}^{-1}$ broadening of these transitions below the detection limit. Such 5 ps lifetimes would correspond to only ≈ 500 vibrations of the OH stretch in the H_2O molecule, a number strikingly small compared to the $\approx 1.6 \times 10^6$ vibrational periods suggested by the lifetime data for $\text{oH}_2\text{-oH}_2\text{O}$ clusters shown in Fig. 6.

Some supporting evidence for this scenario can be found in Fig. 7, which summarizes cluster energy levels with respect to dissociated H_2 and H_2O monomers in the appropriate nuclear spin states. Since predissociation pathways are typically most efficient when energy deposition into translation and rotation is minimized, such effects can be greatly accelerated by near resonances between accurately determined cluster vs. free molecule vibrational levels.^{69–72} As shown in Fig. 7, $\text{oH}_2\text{-pH}_2\text{O}$ in the $|02^+ \rangle$ vibrational state is nearly resonant with (indeed, only 10 cm^{-1} higher than) predissociation into the $\text{H}_2(v=0, j=1) + \text{H}_2\text{O}(|02^+ \rangle)_{000}$ asymptotic levels. In a simple physical picture, this predissociation event could be thought of as corresponding to “intramolecular collisional readjustment” of the relative phases between the two local mode OH stretches in $|02^- \rangle$ to generate the lower frequency $|02^+ \rangle$ vibration. By way of contrast, the $\text{oH}_2\text{-oH}_2\text{O}$ cluster has no vibrationally asymptotic states closer than the $|01^- \rangle|v_{\text{bend}}=2 \rangle$ level, which must be accompanied by simultaneously depositing $\approx 300 \text{ cm}^{-1}$ into rotation and translation. From a Fermi

Golden rule perspective, such highly nuclear spin species dependent densities of final states could be responsible for the requisite 1000-fold acceleration in predissociation rates out of the $|02^- \rangle$ $\text{oH}_2\text{-pH}_2\text{O}$ vs $\text{oH}_2\text{-oH}_2\text{O}$ upper states.

In addition to such large differences in predissociation lifetimes for different nuclear spin states, it is worth briefly investigating reasons for the measurable differences in predissociation lifetimes for Π ($<5(2) \text{ ns}$) and Σ ($15(2) \text{ ns}$) upper states of $\text{oH}_2\text{-oH}_2\text{O}$. Indeed, though covering a substantially different dynamic range, this discussion might offer a useful basis of comparison with overtone studies on rare gas $\text{Ar-pH}_2\text{O}$ complexes, for which the $|02^- \rangle \Pi(1_{01})$ internal rotor state was also found to predissociate on a significantly faster timescale ($\tau_{\text{vp}} \approx 54(2) \text{ ns}$) than the $\Sigma(1_{01})$ state ($\tau_{\text{vp}} \approx 105(8) \text{ ns}$).⁷³ Of particular relevance is that the internal rotor angular momentum projections for both pairs of states in the $\text{H}_2\text{-oH}_2\text{O}$ and $\text{Ar-pH}_2\text{O}$ complexes maintain the *same* H_2O internal rotor level but *vary* between Π ($K=1$) and Σ ($K=0$) character. This may suggest one important dynamical aspect in influencing predissociation rates to be the intramolecular steric factor. By this we mean a probability for achieving geometries where transfer of the initial H_2O stretching vibration to intermolecular bond breaking would be expected to be most facile. For $\text{M-H}_2\text{O}$ clusters, a reasonable case could be made that the propensity for either of the rapidly vibrating OH bonds to align with the intermolecular predissociation axis to represent a measure of such a coordinate.

With the intermolecular wavefunctions from first principles *ab initio* theory and dynamics, we can explore this one step further. Specifically, 2D body fixed angular wavefunction contour plots for the $\Sigma(1_{000})$ $J=0$ and $\Pi(1_{000})$ $J=1$ levels of $\text{oH}_2\text{-oH}_2\text{O}$ in the $|02^- \rangle$ excited state manifold are shown in Fig. 3, with the underlying monomer geometries represented for a number of points. Of particular relevance is the vertical dotted line in each contour at $\beta_{\text{H}_2\text{O}} \approx 128^\circ$, which indicates the locus of all geometries with the OH bond pointing directly toward the H_2 monomer subunit. The wavefunction for the *more slowly* predissociating Σ state peaks *far away* from this line at the global minimum structure with H_2 as donor and H_2O as acceptor, for which both OH bonds of the H_2O monomer point away from H_2 . By way of contrast, the wavefunction for the *more rapidly* predissociating Π state has its maximum amplitude *much nearer* to the alternative hydrogen-bonded structure, i.e., H_2 as acceptor and H_2O as donor, with the donor O–H bond “pointing” more directly toward H_2 . Clearly more theoretical work needs to be done to elucidate this issue further. Nevertheless, this zero order analysis offers a simple and physically motivated picture for why $|02^- \rangle$ OH stretch excitation in $\text{M-H}_2\text{O}$ complexes might be more effective in predissociation dynamics for Π vs. Σ internal rotor states.

As a final comment, such $\text{H}_2\text{-H}_2\text{O}$ potential energy surfaces may have additional relevance toward understanding chemistry in the interstellar medium. One of the most significant problems of interstellar importance is formation of molecular H_2 from H atoms on icy grain surfaces, for which a delicate balance must be struck to occur efficiently. At too high a temperature, the ice mantle will thermally desorb

FIG. 7. Energies (with respect to the $\text{pH}_2(v=0, j=0) + \text{pH}_2\text{O}(|00^+ \rangle)_{000}$ ground state) for $\text{oH}_2\text{-pH}_2\text{O}$, $\text{oH}_2\text{-oH}_2\text{O}$ bound states and nearby $\text{H}_2(v=0, j) + \text{pH}_2\text{O}(|02^- \rangle)_{jkakc}$ and $\text{oH}_2 + \text{oH}_2\text{O}(|02^- \rangle)_{jkakc}$ asymptotic states of these clusters. The lowest spectroscopically accessible level of $\text{oH}_2\text{-pH}_2\text{O}$ ($|02^- \rangle$, $\Pi(1_{01})$) lies only $\approx 10 \text{ cm}^{-1}$ above the dissociation limit to $\text{H}_2(v=0, j=1) + \text{H}_2\text{O}(|02^+ \rangle)_{000}$, which likely promotes rapid, near resonant predissociation dynamics. For $\text{oH}_2\text{-oH}_2\text{O}$ ($|02^- \rangle$, $\Sigma(1_{000})$), on the other hand, the nearest energetically allowed predissociation pathway to form $\text{H}_2(v=0, j=1) + \text{H}_2\text{O}(|01^- \rangle|v_{\text{bend}}=2 \rangle)_{000}$ is non-resonant by $>300 \text{ cm}^{-1}$. This translates into much narrower predissociation linewidths, which makes the IR spectra observable at the current signal to noise.

weakly bound H atoms before they encounter other H atoms on the surface. On the other hand, at too low a temperature, energy barriers for activated hopping limit H atom encounter and Langmuir-Hinshelwood formation of H₂. In fact, careful studies on lab-grown porous amorphous solid water (the most likely form of interstellar surface ice) indicate a rapid drop off in H₂ formation efficiency outside a surface temperature window⁷⁴ between 11 K and 17 K. Interestingly, significant discrepancies exist between models based on laboratory rates vs. H₂ reformation rates observed in molecular clouds,⁷⁵ which may signal fundamental issues yet to be explored. It is our hope that such a benchmark potential surface for the H₂-H₂O interaction may help provide a quantitative step toward a more first principles understanding of H atom recombination dynamics on icy grains.

VII. SUMMARY AND CONCLUSIONS

A combined theoretical and experimental study has been carried out for weakly bound H₂-H₂O dimers. The theoretical calculations are based on a high level *ab initio* potential energy surface in full dimensionality, which has been reduced to a 5D surface in intermolecular coordinates by suitable adiabatic averaging over the full 4 intramolecular degrees of freedom corresponding to a specific H₂ and H₂O vibrational state. Eigenvalues and eigenfunctions of the intermolecular Hamiltonian are then obtained from high level dynamics calculations, which allow for large amplitude quantum motion in 5D. These calculations yield accurate predictions of both bound ground |00⁺) and upper |02⁻) state rovibrational levels, which in conjunction with a dipole moment attached to the H₂O body frame, permit the direct absorption spectra of the H₂-H₂O clusters in the near IR region to be predicted for each of the four possible nuclear spin species: oH₂-oH₂O, oH₂-pH₂O, pH₂-oH₂O, pH₂-pH₂O. These predictions have been compared with experimental spectra of clusters obtained in a slit supersonic expansion and interrogated using a novel triple laser technique, based on (i) IR laser absorption by the cluster in the first overtone region for H₂O, (ii) 193 nm photolysis of the H₂O moiety, and (iii) 308 nm laser induced fluorescence detection of the resulting OH radical.

Agreement for the oH₂-oH₂O nuclear spin species is excellent, with the first principles theoretical spectrum uniformly blue shifted from experimental observation and consistent with a remarkably small 0.195(7) cm⁻¹ residual differential error in the ground vs. excited state H₂-H₂O dissociation energies. Two bands are observed for the oH₂-oH₂O species, a Σ (1,0₀₀) $\leftarrow$ Π (1,1₀₁) band with an upper state predissociation lifetime of 15(2) ns, and a Π (1,0₀₀) $\leftarrow$ Π (1,1₀₁) band, which accesses states which predissociate on a $\leq$ 5(2) ns time scale comparable with experimental resolution. Based on the first principles eigenfunctions, we argue that these differences in predissociation rates are attributed to different propensities for intermolecular alignment of the OH bond along the intermolecular axis and thus different rates for intermolecular vibrational energy transfer into the cluster dissociation coordinate.

While observation and spectral assignment of the oH₂-oH₂O species is unambiguous, the other nuclear spin cluster

modifications are not observed experimentally, despite quantitatively accurate predictions and high expected signal to noise presuming all nuclear spin species are populated statistically. We argue that this is a result of quantum mechanical, kinetic, and dynamical considerations. From a quantum mechanical perspective, the pH₂-(o/p)H₂O clusters are predicted to be more weakly bound by $\approx$ 20 cm⁻¹ than the corresponding oH₂-(o/p)H₂O species. This translates into a chaperone mechanism for collisional displacement of pH₂ by oH₂ to form the more stable oH₂-(o/p)H₂O species, as noted in previous mid IR spectroscopic studies of HOH bend excited clusters. On the other hand, we attribute the surprising lack of observation of the remaining oH₂-pH₂O species to rapid predissociation arising from a near resonant channel ($\Delta E < 30$ cm⁻¹) to form oH₂(j = 1) + pH₂O |02⁺) (0₀₀). In summary, these studies represent a remarkable example of synergistic comparison between first principles *ab initio*/dynamical theory and detailed spectroscopic measurement, targeting a simple van der Waals/hydrogen bonded cluster that may play a crucial role in H₂ molecular formation in interstellar clouds.

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APPENDIX: DERIVATION OF LINE STRENGTH FORMULA

The eigenstates of the Hamiltonian of a weakly bound dimer consisting of two arbitrary, nonlinear, molecules are conveniently computed in the BF basis¹⁵

$$|n, I; J, M\rangle = \chi_n(R) \left[\frac{(2j_A + 1)(2j_B + 1)(2J + 1)}{256\pi^5} \right]^{1/2} \\ \times \sum_{m_A m_B} D_{m_A k_A}^{(j_A)}(\omega_A)^* D_{m_B k_B}^{(j_B)}(\omega_B)^* \\ \times \langle j_A m_A; j_B m_B | j_{AB} K \rangle D_{MK}^{(J)}(\Phi, \Theta, 0)^* \quad (\text{A1})$$

with n labeling the radial basis functions $\chi_n(R)$ and I denoting the set of internal angular quantum numbers $\{j_A, k_A, j_B, k_B, j_{AB}, K\}$. The Euler angles ω_A and ω_B define the orientations of the monomers A and B relative to the BF frame and the angles Θ, Φ are the polar angles of the vector $\mathbf{R}$ with respect to a space-fixed (SF) laboratory frame. This vector $\mathbf{R}$ points from the center of mass of monomer A to that of monomer B and the z -axis of the BF frame was chosen parallel to $\mathbf{R}$. The Wigner functions $D_{mk}^{(j)}(\omega)^*$ are the eigenfunctions of a symmetric rotor and $\langle j_A m_A; j_B m_B | j_{AB} K \rangle$ is a Clebsch-Gordan

coefficient. The overall angular momentum J and its component M on the SF z -axis are exact quantum numbers. The rovibrational wavefunctions $|i, J, M\rangle$ of the dimer are given by

$$|i, J, M\rangle = \sum_{n,I} |n, I; J, M\rangle c_{n,I}^{i,J,M} \quad (\text{A2})$$

with coefficients $c_{n,I}^{i,J,M}$ obtained by diagonalization of the dimer Hamiltonian in the basis of Eq. (A1).

The components of the dipole moment operator with respect to the SF frame are related to those in the BF frame by

$$\mu_m^{SF} = \sum_k \mu_k^{BF}(R, \omega_A, \omega_B) D_{mk}^{(1)}(\Phi, \Theta, 0)^*. \quad (\text{A3})$$

The BF dipole component with $k = 0$ is the component parallel to the dimer z -axis (the vector $\mathbf{R}$) and the components with $k = \pm 1$ are perpendicular to $\mathbf{R}$. The BF components of

the dipole moment operator may be expanded as

$$\mu_k^{BF}(R, \omega_A, \omega_B) = \sum_{\Lambda} d_{\Lambda,k}^{BF}(R) B_{\Lambda,k}^{BF}(\omega_A, \omega_B) \quad (\text{A4})$$

with the same type of angular functions as used in the basis

$$B_{\Lambda,k}^{BF}(\omega_A, \omega_B) = \sum_{M_A, M_B} D_{M_A K_A}^{(L_A)}(\omega_A)^* D_{M_B K_B}^{(L_B)}(\omega_B)^* \times \langle L_A M_A; L_B M_B | L k \rangle \quad (\text{A5})$$

and $\Lambda \equiv \{L_A, L_B, L, K_A, K_B\}$. Since the dipole is a vector, we must use functions with $L = 1$. Since we have assumed that the dipole moment function only depends on the six intermolecular coordinates, the expansion coefficients $d_{\Lambda,k}^{BF}$ depend only on the distance R . In general, they may depend on the intramolecular coordinates as well.

The matrix elements of the dipole moment operator μ^{SF} over the basis functions in Eq. (A1) are

$$\begin{aligned} \langle n', I'; J' M' | \mu_m^{SF} | n, I; J M \rangle &= (-1)^{M'+J_A+J_B+J_{AB}+K_A+K_B} \\ &\times [(2J'+1)(2J+1)(2j'_A+1)(2j'_B+1)(2j_A+1)(2j_B+1)(2j'_{AB}+1)(2j_{AB}+1)]^{1/2} \\ &\times \begin{pmatrix} J' & 1 & J \\ -M' & m & M \end{pmatrix} \sum_k \begin{pmatrix} J' & 1 & J \\ -K' & k & K \end{pmatrix} \\ &\times \sum_{\Lambda} (-1)^{L_A+L_B+L} (2L+1)^{1/2} \langle \chi_{n'}(R) | d_{\Lambda,k}^{BF}(R) | \chi_n(R) \rangle \\ &\times \begin{pmatrix} j'_A & L_A & j_A \\ -k'_A & K_A & k_A \end{pmatrix} \begin{pmatrix} j'_B & L_B & j_B \\ -k'_B & K_B & k_B \end{pmatrix} \begin{pmatrix} j'_{AB} & L & j_{AB} \\ -K' & k & K \end{pmatrix} \left\{ \begin{matrix} j'_A & L_A & j_A \\ j'_B & L_B & j_B \\ j'_{AB} & L & j_{AB} \end{matrix} \right\}, \quad (\text{A6}) \end{aligned}$$

where the expressions in large round brackets are 3-j symbols and the curly brackets denote a 9-j symbol.⁵⁹ This formula is nearly identical to Eq. (16.27) in the book on *Molecular Symmetry and Spectroscopy* by Bunker and Jensen⁶⁰ with the exception of a different phase factor, $(-1)^{j'_A+j'_B+j'_{AB}+K_A+K_B+M'}$ in their formula, which is incorrect.

If we assume that the dipole moment function is purely determined by the (transition) dipole moment on monomer A, it does not depend on the intermolecular distance R , nor on the Euler angles ω_B . The dipole expansion coefficients $d_{\Lambda,k}^{BF}$ become simply

$$d_{\Lambda,k}^{BF} = \delta_{L_B 0} \delta_{K_B 0} \delta_{L_A 1} \delta_{L_A L} \mu_{K_A} \quad (\text{A7})$$

for each value of k , where $\mu_{K_A} \equiv Q_{K_A}^{(1)}$ are the components of the (transition) dipole moment on monomer A, expressed in the local A monomer frame. The symbols δ denote Kronecker deltas. If one (i) substitutes this result into the general formula, (ii) writes the specific 3-j symbol as

$$\begin{pmatrix} j'_B & 0 & j_B \\ -k'_B & 0 & k_B \end{pmatrix} = \delta_{j'_B j_B} \delta_{k'_B k_B} (-1)^{j_B+K_B} (2j_B+1)^{-1/2}, \quad (\text{A8})$$

and (iii) reduces the specific 9-j symbol to a 6-j symbol

$$\left\{ \begin{matrix} j'_A & 1 & j_A \\ j_B & 0 & j_B \\ j'_{AB} & 1 & j_{AB} \end{matrix} \right\} = (-1)^{j_A+j_B+j'_{AB}+1} [3(2j_B+1)]^{-1/2} \left\{ \begin{matrix} j_A & 1 & j'_A \\ j'_{AB} & j_B & j_{AB} \end{matrix} \right\}, \quad (\text{A9})$$

one obtains

$$\begin{aligned}
 & \langle n', I'; J' M' | \mu_m^{SF} | n, I; J M \rangle \\
 &= (-1)^{j_{AB}+j_B+j'_{AB}+k'_A+M'+1} \delta_{n'n} \delta_{j'_B j_B} \delta_{k'_B k_B} \\
 & \times [(2J' + 1)(2J + 1)(2j'_A + 1)(2j_A + 1)(2j'_{AB} + 1)(2j_{AB} + 1)]^{1/2} \\
 & \times \begin{pmatrix} J' & 1 & m \\ -M' & J & M \end{pmatrix} \begin{Bmatrix} j_A & 1 & j'_A \\ j'_{AB} & j_B & j_{AB} \end{Bmatrix} \sum_k \begin{pmatrix} J' & 1 & J \\ -K' & k & K \end{pmatrix} \begin{pmatrix} j'_{AB} & 1 & j_{AB} \\ -K' & k & K \end{pmatrix} \\
 & \times \sum_{K_A} \mu_{K_A} \begin{pmatrix} j'_A & 1 & j_A \\ -k'_A & K_A & k_A \end{pmatrix}.
 \end{aligned} \tag{A10}$$

The same formula is obtained by direct derivation of the transition dipole matrix elements for the simplified case. By way of contrast, the simplifications of Eqs. (A7)–(A9) put into Eq. (16.27) in Ref. 60 yield the incorrect phase factor $(-1)^{j_A+j_B+j'_A+k'_A+M'+1}$.

The H₂-H₂O complex only has five intermolecular degrees of freedom. In our calculation of line strengths of the $|02^- \rangle \leftarrow |00^+ \rangle$ transition in this complex, the transition dipole function (μ) depending only on these five intermolecular coordinates, was defined by averaging the full 9D dipole function over the ground state vibrational wavefunction of H₂ and taking the transition matrix element between the ground state and $|02^- \rangle$ excited state wavefunctions of H₂O. Furthermore, since H₂ is linear, we may substitute $k'_B = k_B = 0$. The local frame chosen on the H₂O monomer has its z -axis along the twofold symmetry axis and the (transition) dipole component with $K_A = 0$ is the $\mu_0 = \mu_z$ component. H₂O is assumed to be in the xz -plane, so that $\mu_y = 0$ and the components with $K_A = \pm 1$ are given by $\mu_{\pm 1} = \mp \mu_x / \sqrt{2}$. The $|02^- \rangle \leftarrow |00^+ \rangle$ vibrational transition in the H₂O monomer studied in this paper is an A-type transition with transition dipole moment μ_x ; we may set $\mu_x = 1$ because we only compute relative intensities. The transition dipole moment for a transition from state $|i, J, M \rangle$ to state $|i', J', M' \rangle$ is then given by

$$d_m^{i,J,M \rightarrow i',J',M'} = \sum_{n',I';n,I} c_{n',I'}^{i',J',M'} c_{n,I}^{i,J,M} \langle n', I'; J' M' | \mu_m^{SF} | n, I; J M \rangle. \tag{A11}$$

Since the molecules are randomly oriented in space and the energies of the states do not depend on the quantum number M , the transition line strength can be obtained in the usual way by summing the square of the transition dipole moment over M' and averaging over M . One can then use the sum relation

$$\sum_{M',M} \begin{pmatrix} J' & 1 & J \\ -M' & m & M \end{pmatrix}^2 = \frac{1}{3} \tag{A12}$$

valid for any value of m ; this permits prediction of the desired line strength $(d^{i,J \rightarrow i',J'})^2$, where $d^{i,J \rightarrow i',J'}$ is obtained from $d_m^{i,J,M \rightarrow i',J',M'}$ by omitting the factor $\begin{pmatrix} J' & 1 & J \\ -M' & m & M \end{pmatrix}$.

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