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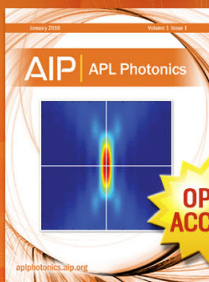
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Quantum theory of atoms in molecules/charge-charge flux-dipole flux models for fundamental vibrational intensity changes on H-bond formation of water and hydrogen fluoride

Arnaldo F. Silva,¹ Wagner E. Richter,¹ Luiz A. Terrabuio,² Roberto L. A. Haiduke,² and Roy E. Bruns^{1,a)}

¹Instituto de Química, Universidade Estadual de Campinas, CP 6154, Campinas, CEP 13083-970, SP, Brazil

²Departamento de Química e Física Molecular, Instituto de Química de São Carlos, Universidade de São Paulo, Av. Trabalhador São-carlense, 400, CP 780, 13560-970 São Carlos, SP, Brazil

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The Quantum Theory of Atoms In Molecules/Charge-Charge Flux-Dipole Flux (QTAIM/CCFDF) model has been used to investigate the electronic structure variations associated with intensity changes on dimerization for the vibrations of the water and hydrogen fluoride dimers as well as in the water-hydrogen fluoride complex. QCISD/cc-pVTZ wave functions applied in the QTAIM/CCFDF model accurately provide the fundamental band intensities of water and its dimer predicting symmetric and *antisymmetric* stretching intensity increases for the donor unit of 159 and 47 km mol⁻¹ on H-bond formation compared with the experimental values of 141 and 53 km mol⁻¹. The symmetric stretching of the proton donor water in the dimer has intensity contributions parallel and perpendicular to its C_{2v} axis. The largest calculated increase of 107 km mol⁻¹ is perpendicular to this axis and owes to equilibrium atomic charge displacements on vibration. Charge flux decreases occurring parallel and perpendicular to this axis result in 42 and 40 km mol⁻¹ total intensity increases for the symmetric and *antisymmetric* stretches, respectively. These decreases in charge flux result in intensity enhancements because of the interaction contributions to the intensities between charge flux and the other quantities. Even though dipole flux contributions are much smaller than the charge and charge flux ones in both monomer and dimer water they are important for calculating the total intensity values for their stretching vibrations since the charge-charge flux interaction term cancels the charge and charge flux contributions. The QTAIM/CCFDF hydrogen-bonded stretching intensity strengthening of 321 km mol⁻¹ on HF dimerization and 592 km mol⁻¹ on HF:H₂O complexation can essentially be explained by charge, charge flux and their interaction cross term. Atomic contributions to the intensities are also calculated. The bridge hydrogen atomic contributions alone explain 145, 237, and 574 km mol⁻¹ of the H-bond stretching intensity enhancements for the water and HF dimers and their heterodimer compared with total increments of 149, 321, and 592 km mol⁻¹, respectively.
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INTRODUCTION

Changes in infrared spectra have furnished some of the most important evidences of hydrogen bond formation.¹ Most notably, the frequencies of the X-H stretching vibrations decrease, their band widths broaden and their intensities increase by as much as an order of magnitude. Since infrared intensities are very sensitive probes of changes in the electronic structures of molecules during vibrational displacements, these dramatic intensity increments have been studied for many years. Most of this research resulted in qualitative explanations for the hydrogen bonding intensity enhancements. Although hydrogen-bonded systems have been the subject of many quantum chemical calculations, few have concentrated on investigating why the H-bond stretching intensity increases so much. In early studies infrared intensities have been interpreted using electro-optical,² equi-

librium charge-charge flux,³ and charge-charge flux-overlap⁴ parameters.

Here attention is focused on the infrared intensities of the water and hydrogen fluoride dimers since ample experimental information exists about their molecular structures.⁵⁻⁸ Zilles and Person⁹ carried out a quantitative theoretical study of H-bonding enhancement in the water dimer using molecular orbital approaches available at that time. Performing a Charge-Charge Flux-Overlap analysis of Hartree-Fock 4-31G wave functions, an increase in charge flux along the direction of the hydrogen bond was found to be the only appreciable change in the polar tensors of monomer and dimer water. This increase was attributed to both charge transfer between water molecules and polarization effects within each unit in the dimer.

Considerable advances have occurred on both the experimental and theoretical fronts to permit more accurate quantitative studies of the infrared intensities of H-bonded molecular complexes. The charge-charge flux-overlap model has been modified¹⁰ and atomic charges determined from atomic

^{a)} Author to whom correspondence should be addressed. Electronic mail: bruns@iqm.unicamp.br

polar tensors have been proposed.¹¹ More recently a method has been proposed to calculate charge fluxes from derivatives of atomic polar tensor elements.¹² Although these models might be expected to describe charge transfer between chemical groups and the localization of excess charge on strategic sites in molecules no explicit parameter describes the effects of polarization of the electronic density such as occurs with lone pairs that are thought to play an important role in hydrogen bonding.

Infrared laser depletion determinations of fundamental intensities of the water dimer in helium droplets have recently been reported.^{13,14} The theoretical calculations of infrared intensities of the water dimer, and its comparison with the water monomer, are currently popular in the literature, as they are used together with thermodynamic parameters to compare different conformations of the water complexes.^{15–21} Although the intensities calculated for the monomer are usually very close to experimental estimates,^{21–27} a problem arises on trying to calculate some of the strongest bands for the dimer. Methods, such as MP2 and Coupled Cluster with large Pople basis sets, provide intensities^{13,20,28} ranging from 250 to 280 km mol⁻¹ for the O-H symmetric stretching intensity of the hydrogen donor unit in the dimer, having large deviations from experimental result of 144 km mol⁻¹. Density Functional Theory (DFT) at the B3LYP/6-311++G(3df,3dp) level¹⁸ has also been applied, yielding even worse intensity values, around 330 km mol⁻¹, for this band. New results in the Computational Chemistry Comparison Benchmark Database²⁰ showed that modern modifications of the configuration interaction method, like QCISD, along with a correlation consistent Dunning basis set (cc-pVDZ), result in a calculated intensity of 170 km mol⁻¹ in a much closer agreement with experiment for this stretching intensity.¹³

Studies on the (HF)₂ complex are less frequent than those available in the literature for the water dimer. However, some of the geometrical parameters have been successfully obtained from the experimental microwave rotational spectra of (HF)₂ and that of its deuterated species,^{7,8} pointing to a bent structure. The Computational Chemistry Comparison Benchmark Database²⁰ is one of the few sources of theoretical infrared information on the hydrogen fluoride dimer. This database shows that perturbation methods, such as MP2, and also DFT combined with large Dunning basis sets yield rather high infrared intensity absorptions, ranging from 432 to 470 km mol⁻¹ for the H-F symmetric stretch.²⁰ Configuration Interaction calculations with more modest Pople basis sets furnish lower intensity values,²⁰ around 408 km mol⁻¹.

To complement the results for the water and hydrogen fluoride dimers, the intensities of the HF:H₂O heterodimer were also investigated. Rotational spectra of the gas phase HF:H₂O complex have been used to partially determine its equilibrium geometry.^{29,30}

In this work, the infrared intensity enhancements observed in these dimers are investigated at the QCISD level with correlation consistent Dunning basis sets using the Quantum Theory of Atoms In Molecules (QTAIM)^{31,32}/Charge-Charge Flux-Dipole Flux (CCFDF) model^{33,34} recently developed by our group. The CCFDF model results in intensity contributions owing to electronic

structure changes for vibrations that can all be interpreted classically as movements of equilibrium atomic charges and changes in atomic charges and atomic dipoles during the vibration. The changes in the atomic dipoles can be expected to describe changes in the electronic density polarizations that could be important for explaining infrared intensity enhancements on hydrogen bonding. Their precise characterizations in the water dimer and other complexes are expected to be important for studies on intermolecular vibrational coupling³⁵ and helpful in attempts to determine a “long-sought universal model” for water.³⁶

CALCULATIONS

Electronic structure calculations were carried out with GAUSSIAN03³⁷ on an AMD 64 Opteron workstation. The geometries of both the monomers and dimers were optimized, starting from the experimental values,^{5–8,29,30} at the QCISD level with cc-pVXZ (X = D,T,Q) basis sets and the CCSD(T) level with a cc-pVQZ-mod set, generating wave functions that were used for further calculations. This modified set (cc-pVQZ-mod) was obtained by the removal of the function with the largest angular momentum value of each atom. For geometry optimization the Basis Set Superposition Error (BSSE)³⁸ for the dimers were corrected using the Counterpoise Method.³⁹ The infrared fundamental intensities were obtained at all the above levels. The MORPHY98⁴⁰ program provided the atomic charges and atomic dipoles from QTAIM. These atomic quantities were used by the PLACZEK⁴¹ program to calculate the molecular dipole moment derivatives, as well as their charge, charge flux and dipole flux contributions.

The infrared intensity of the *k*th fundamental band is proportional to the sum of squares of the Cartesian components of the dipole moment derivative with respect to this normal coordinate, Q_k ,

$$A_k = \frac{N\pi}{3c^2} \left[\left(\frac{\partial p_x}{\partial Q_k} \right)^2 + \left(\frac{\partial p_y}{\partial Q_k} \right)^2 + \left(\frac{\partial p_z}{\partial Q_k} \right)^2 \right]. \quad (1)$$

The vibrations for most molecules with high symmetry are accompanied by dipole moment changes that are restricted to one of the Cartesian coordinate axis, $\sigma = x, y,$ or z . However, the water dimer experiences significant vibrational dipole moment changes in at least two directions.

The dipole moment derivative with respect to the *k*th normal coordinate^{42,43} is

$$\frac{\partial p_\sigma}{\partial Q_k} = \sum_i q_i \frac{\partial \sigma_i}{\partial Q_k} + \sum_i \frac{\partial q_i}{\partial Q_k} \sigma_i + \sum_i \frac{\partial m_{i,\sigma}}{\partial Q_k}. \quad (2)$$

The first term, the charge contribution $(\partial p_\sigma / \partial Q_k)_C$, is a weighted sum of atomic charges for which the weights correspond to the relative atomic displacements for the *k*th normal coordinate. The second is a weighted sum of charge changes for which the loadings are the equilibrium Cartesian coordinates of the atoms, designated as the charge flux contribution $(\partial p_\sigma / \partial Q_k)_{CF}$. The final term is a simple sum of the derivatives of the σ th Cartesian component of the atomic dipoles with respect to the *k*th normal coordinate, the

dipole flux contribution $(\partial p_\sigma / \partial Q_k)_{DF}$. As such, the QTAIM Charge-Charge Flux-Dipole Flux (CCFDF) model partitions each Cartesian component of the total dipole moment derivative into charge (C), charge flux (CF), and dipole flux (DF) contributions,

$$\frac{\partial p_\sigma}{\partial Q_k} = \left(\frac{\partial p_\sigma}{\partial Q_k} \right)_C + \left(\frac{\partial p_\sigma}{\partial Q_k} \right)_{CF} + \left(\frac{\partial p_\sigma}{\partial Q_k} \right)_{DF}. \quad (3)$$

After substitution in Eq. (1), the CCFDF contributions to the infrared intensity are

$$\begin{aligned} A_k = & \left(\frac{N\pi}{3c^2} \right) \sum_\sigma \left[\left(\frac{\partial p_\sigma}{\partial Q_k} \right)_C^2 + \left(\frac{\partial p_\sigma}{\partial Q_k} \right)_{CF}^2 \right. \\ & + \left(\frac{\partial p_\sigma}{\partial Q_k} \right)_{DF}^2 + 2 \left(\frac{\partial p_\sigma}{\partial Q_k} \right)_C \left(\frac{\partial p_\sigma}{\partial Q_k} \right)_{CF} \\ & \left. + 2 \left(\frac{\partial p_\sigma}{\partial Q_k} \right)_C \left(\frac{\partial p_\sigma}{\partial Q_k} \right)_{DF} + 2 \left(\frac{\partial p_\sigma}{\partial Q_k} \right)_{CF} \left(\frac{\partial p_\sigma}{\partial Q_k} \right)_{DF} \right]. \quad (4) \end{aligned}$$

The first three squared terms represent the charge, charge flux, and atomic dipole flux contributions to the k th fundamental vibrational intensity. The last three terms correspond to interactions between charge, charge flux, and dipole flux contributions and can be positive when both derivative contributions are of the same sign, reinforcing the total intensity, or negative when the contributions have opposite signs, decreasing the total intensity.

The summation result of this intensity partition over Cartesian directions can be expressed as

$$\begin{aligned} A_k = & [A_k(Cx C) + A_k(CFx CF) \\ & + A_k(DFx DF) + A_k(2Cx CF) \\ & + A_k(2Cx DF) + A_k(2CFx DF)]. \quad (5) \end{aligned}$$

The rearranging and grouping of appropriate terms in Eq. (2) permits an even more detailed CCFDF analysis for which atomic contributions to the infrared intensities can be assessed. The dipole moment derivative in Eq. (2) can be partitioned into three kinds of atomic terms. The first of them is associated with derivative contributions owing to the i th atomic equilibrium charge displacement occurring for the

normal coordinate, $q_i(\partial \sigma_i / \partial Q_k) = (\partial p_\sigma / \partial Q_k)_{C(i)}$. The third term in Eq. (2) provides contributions from each atomic dipole change for the normal coordinate displacements, $(\partial m_{i,\sigma} / \partial Q_k) = (\partial p_\sigma / \partial Q_k)_{DF(i)}$. The charge derivative of the second term in Eq. (2) can be transformed into atomic Cartesian coordinates,

$$\sum_i^N \left(\partial q_i / \partial Q_k \right) \sigma_i = \sum_i^N \left[\sum_j^{3N} \left(\partial q_i / \partial \sigma_j \right) \left(\partial \sigma_j / \partial Q_k \right) \right] \sigma_i, \quad (6)$$

by using elements of the L matrix.^{42,43} Thus, grouping the terms corresponding to the Cartesian coordinate displacement of each atom j results in

$$\begin{aligned} \sum_i^N \left(\partial q_i / \partial Q_k \right) \sigma_i &= \sum_j^{3N} \left[\sum_i^N \left(\partial q_i / \partial \sigma_j \right) \sigma_i \right] \left(\partial \sigma_j / \partial Q_k \right) \\ &= \sum_j^N \left(\partial p_\sigma / \partial Q_k \right)_{CF(j)} = \left(\partial p_\sigma / \partial Q_k \right)_{CF}. \quad (7) \end{aligned}$$

The term in brackets represents the change in dipole moment from all atomic charge changes in the molecule on a Cartesian displacement of the j th atom. This derivative is weighted by the importance of the j th Cartesian displacement in the k th normal coordinate.

Then, using a common index to represent the atoms since each sum in these equations is over all the atoms, and substituting into Eq. (1) furnishes atomic contributions to the intensity,

$$\begin{aligned} A_k = & \left(\frac{N\pi}{3c^2} \right) \sum_\sigma \left\{ \sum_i^N \left[\left(\partial p_\sigma / \partial Q_k \right)_{C(i)} \right. \right. \\ & \left. \left. + \left(\partial p_\sigma / \partial Q_k \right)_{CF(i)} + \left(\partial p_\sigma / \partial Q_k \right)_{DF(i)} \right] \right\}^2 \quad (8) \end{aligned}$$

and

$$A_k = \sum_\sigma \left[\sum_i^N A_{k(i)}^\sigma + \sum_{i < j}^N \sum A_{k(i,j)}^\sigma \right], \quad (9)$$

where

$$\begin{aligned} A_{k(i)}^\sigma = & \left(\frac{N\pi}{3c^2} \right) \left[\left(\partial p_\sigma / \partial Q_k \right)_{C(i)}^2 + \left(\partial p_\sigma / \partial Q_k \right)_{CF(i)}^2 + \left(\partial p_\sigma / \partial Q_k \right)_{DF(i)}^2 \right. \\ & + 2 \left(\partial p_\sigma / \partial Q_k \right)_{C(i)} \left(\partial p_\sigma / \partial Q_k \right)_{CF(i)} + 2 \left(\partial p_\sigma / \partial Q_k \right)_{C(i)} \left(\partial p_\sigma / \partial Q_k \right)_{DF(i)} \\ & \left. + 2 \left(\partial p_\sigma / \partial Q_k \right)_{CF(i)} \left(\partial p_\sigma / \partial Q_k \right)_{DF(i)} \right] \quad (10) \end{aligned}$$

and

$$\begin{aligned} A_{k(i,j)}^\sigma = & \frac{N\pi}{3c^2} \left[2 \left(\partial p_\sigma / \partial Q_k \right)_{C(i)} \left(\partial p_\sigma / \partial Q_k \right)_{C(j)} + 2 \left(\partial p_\sigma / \partial Q_k \right)_{C(i)} \left(\partial p_\sigma / \partial Q_k \right)_{CF(j)} \right. \\ & \left. + 2 \left(\partial p_\sigma / \partial Q_k \right)_{C(i)} \left(\partial p_\sigma / \partial Q_k \right)_{DF(j)} + 2 \left(\partial p_\sigma / \partial Q_k \right)_{CF(i)} \left(\partial p_\sigma / \partial Q_k \right)_{C(j)} \right] \end{aligned}$$

$$\begin{aligned}
& + 2 \left(\frac{\partial p_\sigma}{\partial Q_k} \right)_{CF(i)} \left(\frac{\partial p_\sigma}{\partial Q_k} \right)_{CF(j)} + 2 \left(\frac{\partial p_\sigma}{\partial Q_k} \right)_{CF(i)} \left(\frac{\partial p_\sigma}{\partial Q_k} \right)_{DF(j)} \\
& + 2 \left(\frac{\partial p_\sigma}{\partial Q_k} \right)_{DF(i)} \left(\frac{\partial p_\sigma}{\partial Q_k} \right)_{C(j)} + 2 \left(\frac{\partial p_\sigma}{\partial Q_k} \right)_{DF(i)} \left(\frac{\partial p_\sigma}{\partial Q_k} \right)_{CF(j)} \\
& + 2 \left(\frac{\partial p_\sigma}{\partial Q_k} \right)_{DF(i)} \left(\frac{\partial p_\sigma}{\partial Q_k} \right)_{DF(j)} \Big]. \tag{11}
\end{aligned}$$

Finally, summing over the Cartesian directions and using the notation of Eq. (5),

$$\begin{aligned}
A_k(j) = & [A_k(C_j x C_j) + A_k(CF_j x CF_j) + A_k(DF_j x DF_j) + A_k(2C_j x CF_j) \\
& + A_k(2C_j x DF_j) + A_k(2CF_j x DF_j)] \tag{12}
\end{aligned}$$

and

$$\begin{aligned}
A_k(i, j) = & A_k(2C_i x C_j) + A_k(2C_i x CF_j) + A_k(2C_i x DF_j) + A_k(2CF_i x C_j) + A_k(2CF_i x CF_j) \\
& + A_k(2CF_i x DF_j) + A_k(2DF_i x C_j) + A_k(2DF_i x CF_j) + A_k(2DF_i x DF_j), \tag{13}
\end{aligned}$$

where the sub-indices represent the atoms.

RESULTS AND DISCUSSION

Water monomer and dimer

The Cartesian coordinate system used for both the water monomer and dimer is shown in Figure 1. Table I contains the experimental values of the fundamental frequencies and infrared intensities for water and its dimer as well as the intensities calculated using the QCISD/cc-pVXZ ($X = D, T$ and $Q_{(mod)}$) and CCSD/cc-pVQZ $_{(mod)}$ approaches. The monomer experimental intensities²¹⁻²⁷ are in better agreement with the QCISD/cc-pVTZ results having only a 2 km mol⁻¹ root mean square (rms) error, within the estimated 4 km mol⁻¹ experimental error and well below those obtained from the other wave functions. The QCISD/cc-pVTZ values for the dimer have an rms error of 14 km mol⁻¹ compared to the experimental values.^{13,14} The agreement is excellent since the estimated experimental errors are $\pm 20\%$ for all bands except for the small symmetric stretching intensity of the water acceptor molecule for which the expected error is larger, $\pm 40\%$. The other wave functions have rms errors about three times the error of the QCISD/cc-pVTZ result.

Table II contains the QTAIM/CCFDF contributions of Eqs. (4) and (5) for the monomer and dimer along the y and z axes of the Cartesian coordinate system for the three fun-

damental bands of the water donor molecule as obtained in QCISD/cc-pVTZ calculations. The total intensities calculated from these CCFDF parameters are a little different from those obtained directly from the wave function owing to numerical errors. The CCFDF contributions for the acceptor water intensities are not included in this table since their values are very similar to those of the monomer, although their Cartesian directions are different.

The symmetric stretching (BD) intensity contributions are given at the top of Table II. This intensity is often referred to as the H-bond stretching intensity and experiences an enhancement of 141 km mol⁻¹ in the H-bonded complex from its small 3 km mol⁻¹ experimental monomer value. The calculated QCISD/cc-pVTZ enhancement in Table II, 149 km mol⁻¹ is very close to this experimental observation, so one can expect that the monomer and dimer QCISD/cc-pVTZ wave functions contain accurate information for understanding their electronic structure changes for vibrations.

As can be seen in Table II, there are two distinct contributions to this intensity strengthening, one along y, 107 km mol⁻¹, and the other in the z direction, 45 km mol⁻¹. Comparing the monomer and dimer CCFDF contributions for the z direction, the contributions associated with charge flux show the largest changes. The charge, charge flux and

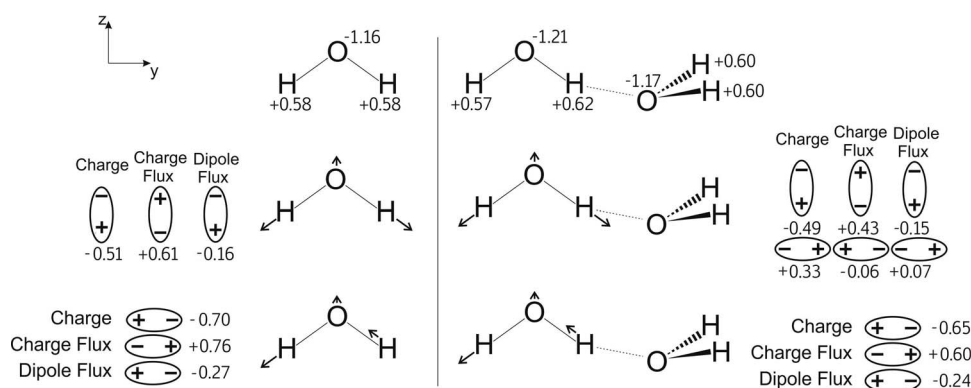


FIG. 1. Cartesian coordinate system and orientations of the water monomer and dimer, equilibrium QCISD/cc-pVTZ QTAIM charges and dipole moment derivative contributions for their symmetric and antisymmetric stretching vibrations.

TABLE I. Experimental and theoretical infrared fundamental intensities of water and HF monomer and dimers.

Frequencies (cm ⁻¹)		Intensities (km mol ⁻¹)				Experimental ^a
		QCISD		CCSD		
		cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pVQZ-mod	
Water monomer						
δ	1595	56	66	70	70	63 ± 7.5
ν (sym.)	3652	4	4	5	5	3 ± 0.4
ν' (antisym.)	3756	22	42	52	53	43 ± 1.5
RMS		13	2	7	7	...
Water dimer						
δ (AD) ^b	...	73	74	84	85	...
δ (DD) ^b	...	44	48	44	46	...
ν (BD)	3597 ^c	223	163	218	224	144 ^d
ν (SA)	3654 ^c	8	9	10	10	5 ^e
ν' (FD)	3730 ^c	97	89	101	97	96 ^d
ν' (AA)	3749 ^c	62	64	74	75	44 ^d
RMS		41	14	41	43	...
Hydrogen fluoride monomer						
ν	4138		102			104
Hydrogen fluoride dimer						
ν (bridge)	4127		381			...
ν	4176		106			...

^aAverage and standard deviations of data in Refs. 21–27.

^bDD (donor deformation), AD (acceptor deformation), BD, FD, SA, and AA. The last four symbols are from Ref. 13.

^cEstimated error of ± 4 cm⁻¹.

^dEstimated error of 20%.

^eEstimated error of 40%.

dipole flux contributions to the dipole moment derivatives of both the monomer and dimer are schematized in Figure 1. On comparing the monomer with the dimer one can see that the only substantial change in the z direction of the dipole moment derivative is due to a decrease in the charge flux from $+0.61$ eu^{-1/2} to $+0.43$ eu^{-1/2}. However, the intensity is related to the squares and cross products of the charge, charge flux, and dipole flux derivative terms as given in Eq. (4). Of the intensity contributions given in Table II the largest changes on dimerization occur for the charge flux and the charge–charge flux interaction terms. The latter is negative because the charge and charge flux changes have opposite polarities. This charge flux decrease is largely cancelled by the increase in the charge–charge flux interaction contribution. So even though the dipole flux provides a small intensity contribution for both the monomer and dimer it is important in determining the intensity increase along the z-axis on dimerization owing mostly to the charge flux–dipole flux interaction term. In fact the sum of the dipole flux, charge–dipole flux and charge flux–dipole flux terms is 47 km mol⁻¹ larger in the dimer than in the monomer compared with the 42 km mol⁻¹ total CCFDF intensity increase calculated along the z-axis.

The largest calculated contribution to the intensity enhancement of the H-bond stretching, 107 km mol⁻¹, comes from the y-direction and is more than double that found along the z-direction. The charge contribution of 106 km mol⁻¹ is much larger than the charge flux and dipole flux terms as well as their interaction terms and accounts for almost all of this predicted intensity increase. This can be understood observing the equilibrium charge difference for the hydrogen atoms

in the dimer shown in Figure 1. This charge asymmetry is not observed in the monomer at the equilibrium geometry and during the symmetric stretching vibration. Fig. 1 illustrates that the large intensity increase results from the charge contribution of $+0.33$ eu^{-1/2} to the dipole moment derivative along the y-axis since the two flux contributions are small and of opposite sign. So the charge contribution accounts for about 70% of the predicted intensity enhancement for the H-bond symmetric stretch.

The dipole moment derivative contributions for the anti-symmetric stretching mode (FD) involving the bridge H atom are also shown in Figure 1. As for the symmetric stretching mode (BD) along the z-axis the predominant change occurs for the charge flux contribution along the y-axis which diminishes from $+0.76$ eu^{-1/2} in the monomer to $+0.60$ eu^{-1/2} in the dimer. Again the charge, charge flux and their interaction contribution, given in Table II, largely cancel one another and the dipole flux terms are important in determining the total intensity. The sum of the dipole flux, charge–dipole flux and charge flux–dipole flux terms is 41 km mol⁻¹ higher in the dimer than in the monomer, close to the total CCFDF intensity increase of 43 km mol⁻¹ calculated from the QCISD/cc-pVTZ wave function. The experimental increase is 53 km mol⁻¹, the intensity of the dimer being about double that of the monomer.

Experimental intensities for the bending mode (DD–Donor Deformation) of the donor water in the dimer are not available. The QCISD/cc-pVTZ wave functions predict a very small intensity decrease for this deformation that essentially involves displacements of the donor water atoms.

TABLE II. Contributions along the y and z Cartesian directions to the total intensities of the water monomer and the dimer donor water fundamental bands and their CCFDF decompositions from QCISD/cc-pVTZ calculations.

	Symmetric stretching			
	z	z	y	Sum (z+y)
	Monomer	Dimer (BD) ^a	Dimer (BD) ^a	Dimer (BD) ^a
Charge	252	231	106	336
Charge flux	360	175	4	179
Dipole flux	25	23	4	27
Charge-charge flux	-602	-402	-41	-443
Charge-dipole flux	158	145	43	187
Charge flux-dipole flux	-189	-126	-8	-134
Total intensity	4	45	107	153
	Antisymmetric stretching			
	y	z	y	Sum (z+y)
	Monomer	Dimer (FD) ^a	Dimer (FD) ^a	Dimer (FD) ^a
Charge	478	19	415	434
Charge flux	563	69	356	425
Dipole flux	68	5	56	60
Charge-charge flux	-1037	-72	-769	-841
Charge-dipole flux	361	18	304	322
Charge flux-dipole flux	391	-35	-281	-316
Total intensity	41	3	80	84
	Angular bending			
	z	z	y	Sum (z+y)
	Monomer	Dimer (DD) ^a	Dimer (DD) ^a	Dimer (DD) ^a
Charge	486	474	4	478
Charge flux	45	37	1	37
Dipole flux	52	78	0	78
Charge-charge flux	-294	-263	-3	-266
Charge-dipole flux	-319	-385	-1	-386
Charge flux-dipole flux	96	107	0	107
Total intensity	66	47	1	49

^aDB, FD, and DD have been defined in Table I.

Table III contains the values of the atomic contributions for the fundamental modes of the water monomer and dimer. Electronic density changes involving the bridge hydrogen by far provide the predominant contribution to the symmetric stretching (BD) intensity of the proton donor unit, 156 km mol⁻¹, close to the total intensity value. For comparison, each hydrogen atom only contributes 11 km mol⁻¹ to the monomer intensity. The 145 km mol⁻¹ intensity increase on dimerization owing to the bridge hydrogen CCFDF terms is about the same as the 141 km mol⁻¹ experimental intensity increase given in Table I. Interestingly, electronic changes on the free hydrogen and the oxygen atoms of the proton donor molecule as well their cross terms have negligible intensity effects on the dimer so the often used phrase, “H-bond stretching intensity enhancement,” indeed seems appropriate for this mode.

The atomic contributions to the antisymmetric stretching (FD) intensity of the donor molecule are given in the sixth column of Table III. The bridge H atom also accounts for about half (24 km mol⁻¹) of the total calculated CCFDF intensity increase (43 km mol⁻¹) of the antisymmetric stretching intensity of the water donor. The largest dimer contributions are

from its hydrogen atoms and the bridge hydrogen interactions with its neighboring oxygen atom and the free hydrogen.

The last columns of this table contain atomic contributions to both of the bending deformation (DD and AD) intensities. The QCISD/cc-pVTZ wave functions predict very similar intensities for these vibrations, 48 and 74 km mol⁻¹, close to the CCFDF values in the table. Their sum, 122 km mol⁻¹ is about twice the calculated monomer intensity, 131 km mol⁻¹. Also all the CCFDF contributions for the monomer and dimer are about the same as can be seen in Table II. This is also true for the atomic contributions of both bending vibrations. So the electronic structure changes of both water molecules in the dimer are very similar to those in the isolated water molecule.

As stated earlier, the CCFDF contributions of the acceptor water stretching vibrations are similar to those of a free water molecule. The atomic intensity contributions to the symmetric stretch of the acceptor water (SA) are contained in the fourth column of Table III. The hydrogen atoms of the donor unit have intensity contributions for this vibration that are much smaller than those for the monomer whereas the major contributions to this intensity come from the acceptor

TABLE III. Atomic contributions to infrared intensities of the fundamental bands for water monomer and dimer (km mol^{-1}) from QCISD/cc-pVTZ calculations.

	Symmetric stretches			Antisymmetric stretches			Bending deformation		
	Mon	Dim (BD) ^a	Dim (SA) ^b	Mon	Dim (FD) ^a	Dim (AA) ^b	Mon	Dim (DD) ^a	Dim (AD) ^b
H(BH) ^a	11	156	2	8	32	0	33	31	1
O(D)	0	1	0	1	1	0	1	1	0
H(FH)	11	3	0	8	11	0	33	30	1
H(A)	11	0	17	8	0	15	33	1	31
O(A)	0	0	0	1	0	1	1	0	1
H(A)	11	0	16	8	0	15	33	1	31
H(BH)O(D)	1	19	0	4	11	0	5	3	0
H(BH)O(A)	...	2	-2	...	0	0	...	-1	1
H(BH)H(FH)	-19	-34	-1	16	25	0	-11	-22	-1
H(BH)H(A)	...	4	-3	...	0	0	...	-7	8
H(BH)H(A)	...	4	-3	...	0	0	...	-7	5
O(D)O(A)	...	0	0	...	0	0	...	0	0
O(D)H(FH)	1	-1	0	4	7	0	5	7	0
O(D)H(A)	...	0	0	...	0	0	...	0	0
O(D)H(A)	...	0	0	...	0	0	...	0	0
O(A)H(A)	...	0	0	...	0	0	...	2	-1
O(A)H(A)	1	0	2	4	0	7	5	0	6
O(A)H(A)	1	0	2	4	0	7	5	0	6
H(FH)H(A)	...	-1	1	...	0	0	...	5	-4
H(FH)H(A)	...	-1	1	...	0	0	...	5	-4
H(A)H(A)	-19	-1	-24	16	0	18	-11	0	-10
Total ^b	7	153	9	81	84	62	133	49	72

^aBH = bridge hydrogen, FH = free hydrogen, D = donor, and A = acceptor.

^bTotal pertains to two isolated water molecules.

water hydrogen atoms. The total CCFDF intensity of 9 km mol^{-1} is equal to the 9 km mol^{-1} intensity value in Table I calculated directly from the QCISD/cc-pVTZ wave function. The experimental value of this intensity in the same table is also small, 5 km mol^{-1} . The atomic contributions for the antisymmetric stretch of the acceptor water (AA) show a similar pattern.

Table IV contains the bridge hydrogen value of the dimer donor partitioned into CCFDF intensity contributions. As found for the total intensity the charge and charge flux contributions are more important on the bridge hydrogen than its dipole flux for the symmetric stretch of both monomer and water donor of the dimer. However, this does not imply that the dipole flux can be ignored for calculating the bridge atom intensity contribution. The charge, charge flux and the charge-charge flux interaction contributions account for a 53 km mol^{-1} intensity increase whereas the sum of the terms involving the dipole flux sum to about twice that amount, 92 km mol^{-1} .

It is of interest to compare our *ab initio* results for the water dimer with those of Torii³⁵ for 28 and 30 molecule water clusters at the DFT B3LYP/6-31+G(2df,p) level. This study focused on a central water molecule with tetrahedral symmetry and double donor-double acceptor interactions with its neighbors. Based on integrated electron densities the intermolecular charge flux was determined to be almost twice as large as the intramolecular charge flux and results from delocalization of electron density from a proton acceptor molecule to the donor molecule with the stretched OH bond.

Within the QTAIM formalism zero-flux surfaces define the boundaries of atoms that satisfy the virial theorem. The electron density of each atom can be integrated and analysis can be made of intra- and intermolecular charge fluxes. At the QCISD/cc-pVTZ level stretching the H-bonded OH bond of the dimer donor results in a localized transfer of $+0.008e$ from the donor oxygen to the stretched hydrogen atom. This localized charge change is similar to the one occurring in free water except that $+0.010e$ is transferred. This is consistent with the smaller charge flux contributions to the H-bond stretching intensities in the dimer than in the monomer given in Table II for both the symmetric and antisymmetric

TABLE IV. CCFDF contributions of the bridge hydrogen atom to the fundamental infrared intensities of the water and hydrogen fluoride monomers, the donor molecules of their dimers and of the HF:H₂O heterodimer (km mol^{-1}) from QCISD/cc-pVTZ calculations.

	H ₂ O		HF		
	H ₂ O (Sym. Str.)	(Sym. Str.) dimer	HF	dimer	HF:H ₂ O
Charge	158	287	501	495	521
Charge flux	205	99	123	21	5
Dipole flux	22	26	3	1	2
Charge-charge flux	-358	-329	-497	-198	68
Charge-dipole flux	119	173	-72	11	67
Charge flux-dipole flux	-135	-101	36	0	4
Total intensity	11	156	94	330	668
Δ	...	145	...	236	574

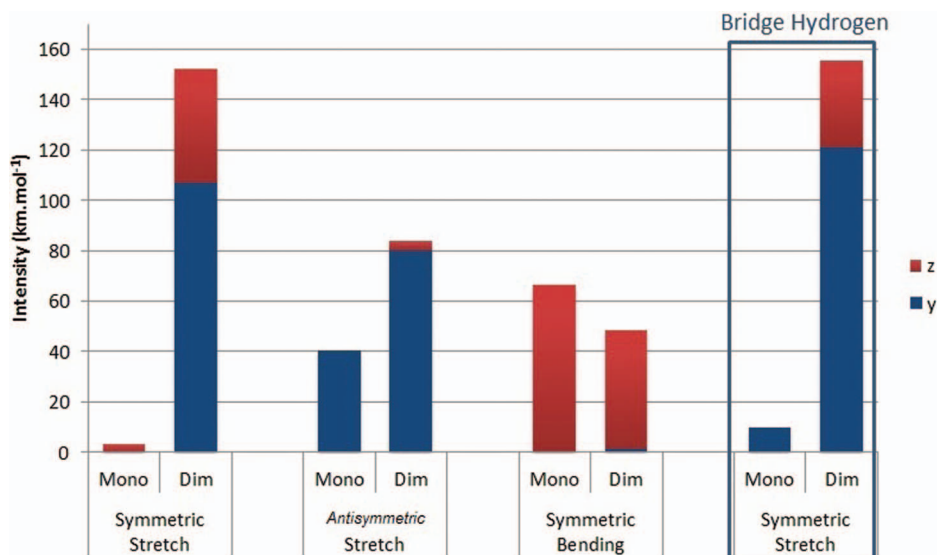


FIG. 2. Bar graph with the contributions along the y and z Cartesian components for the total intensities of the donor water vibrations. The results are shown for both the monomer and the dimer. The bridge (i.e., involved in the hydrogen bond) hydrogen is highlighted as it alone can explain most of intensity enhancement phenomenon.

stretching vibrations. A B3LYP/6-31+G(2df,p) calculation also resulted in a localized charge flux involving that stretched OH bond in the dimer except that only about one half of the *ab initio* result was transferred. On making this comparison it must be remembered that the calculational level of the dimer is much different than that of the water cluster. B3LYP/6-31+G(2df,p) calculations predict a symmetric stretching intensity of the donor unit of the water dimer of 307 km mol⁻¹ compared with the QCISD/cc-pVTZ value of 163 km mol⁻¹ and an experimental value of 144 km mol⁻¹. But it is encouraging that both the DFT and *ab initio* results are in qualitative agreement about the nature of the electron density changes for the H-bond stretching vibrations in the dimer.

Figure 2 summarizes the intensity changes on H-bond formation partitioned into parallel and perpendicular contributions relative to the C_{2v} symmetry axis of the water donor molecule. The symmetric stretching intensity enhancement perpendicular to this axis is mostly due to charge asymmetry that is created on H-bond formation. The smaller enhancement owing to dipole moment changes from charge flux contributions parallel to the symmetry axis is of similar size to the increase in the antisymmetric stretching intensity perpendicu-

lar to it. The intensities calculated for the bending vibration of the water donor and for all of the water acceptor fundamentals in the dimer are about the same as those in the monomer. Finally the bridge hydrogen atom contribution can account for almost all of the H-bond intensity increment for the symmetric stretching of the donor water.

HF monomer and dimer

Figure 3 contains the Cartesian coordinate system and orientations of the HF monomer and dimer. Their QCISD/cc-pVTZ intensity values are included in Table I. The experimental monomer intensity of 104 km mol⁻¹ is within 2 km mol⁻¹ of the QCISD/cc-pVTZ values. The theoretical prediction for the stretching band intensity of the HF donor in the dimer is almost four times the one calculated for the monomer, although the HF acceptor vibration has an intensity value almost the same as that for the monomer. As can be seen in this figure the most predominant change for the HF stretch of the proton donor occurs for the charge flux which is smaller in magnitude in the dimer, -0.18 eu^{-1/2} than in the monomer,

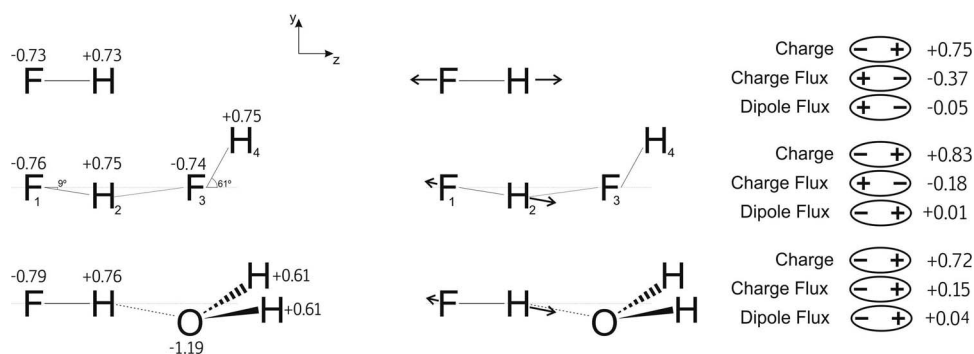


FIG. 3. Cartesian coordinate system and orientations of the HF monomer and dimer, equilibrium QCISD/cc-pVTZ QTAIM charges and dipole moment derivative contributions for their stretching vibrations.

TABLE V. Total CCFDF contributions to the infrared intensities of the HF monomer and for the donor molecule in its dimer and in the HF:H₂O heterodimer (km mol⁻¹) from QCISD/cc-pVTZ calculations.

	HF	HF dimer (PD)	HF:H ₂ O (PD)
Charge	555	677	505
Charge flux	137	31	21
Dipole flux	3	0	1
Charge-charge flux	-551	-291	122
Charge-dipole flux	-80	9	44
Charge flux-dipole flux	40	-2	2
Total intensity	104	425	696
Δ	...	321	592

-0.37 eu^{-1/2}. The charge contribution has a moderate increase on dimerization, from +0.75 eu^{-1/2} in the monomer to +0.83 eu^{-1/2} in the dimer. The dipole flux contributions are small for both. Table V contains the CCFDF contributions to the monomer and dimer intensities. The calculated intensity increase of about 300 km mol⁻¹ can be accounted for mostly by three major factors, an increase in the charge contribution (122 km mol⁻¹), a decrease in the charge flux (106 km mol⁻¹) and an increment in the charge-charge flux interaction term (260 km mol⁻¹). These changes correspond to an increase of 276 km mol⁻¹ in the dimer and accounts for most of the total increase, 321 km mol⁻¹.

Table IV also contains the CCFDF contributions for the bridge hydrogen. All the hydrogen atom contributions for the monomer are very similar to the total CCFDF contributions. The bridge hydrogen accounts for a large portion of the intensity increase owing to a decrease in its charge flux terms and a concomitant large increase in the charge-charge flux interaction. In fact, the charge flux decrease on the bridge hydrogen is 102 km mol⁻¹, which is almost exactly the same as the total charge flux decrease for the H-bonded complex of 106 km mol⁻¹. The bridge atom charge contribution remains almost unchanged on H-bond formation. As can be seen in Figure 3 the largest changes obtained for the equilibrium charges on complex formation occur for the terminal fluorine atom that does not directly participate in the H-bond. This fluorine becomes more negatively charged since the proton acceptor donates electronic charge to the HF donor molecule. As in the water dimer, the bridge hydrogen becomes more positively charged. Moderate atomic intensity contributions arise from CCFDF cross terms for the hydrogen and fluorine atoms of the HF donor molecule and the donor H - acceptor H atoms, 28 and 52 km mol⁻¹, respectively. However, these values are much smaller than the bridge atom contribution of 330 km mol⁻¹. Overall, the effect of electron density rearrangements on the H-bonded stretching intensity in the HF dimer appears to be similar to the one calculated for the water dimer, which has a bridge atom contribution of 156 km mol⁻¹ and smaller contributions of 19 and -34 km mol⁻¹ from the OH and HH donor molecule cross terms.

In summary, most of the intensity enhancement for the H-bond stretching mode in the HF dimer can be explained by sums of the charge, charge flux and charge-charge flux contributions in both the monomer and dimer, contrary to the very

small values for these sums for the H-bonded symmetric and antisymmetric stretching modes in the water monomer and dimer. On the other hand, the atomic contributions to the intensities in both dimers follow the same pattern.

The HF:H₂O heterodimer

Figure 3 also contains the dipole moment contributions for the HF:H₂O heterodimer. The charge contributions are about the same and the dipole flux contributions are small in both the monomer and heterodimer. The only substantial change occurs for the charge flux. In fact, contrary to the water and HF dimers, the charge flux polarity changes from monomer to dimer. So the charge-charge flux interaction contribution has the same sign as the charge and charge flux ones. Their sum in the heterodimer of 648 km mol⁻¹ compared with 141 km mol⁻¹ in the HF monomer corresponds to 507 km mol⁻¹ or 86% of the total intensity increase. The dipole flux contributions are very small in both the HF monomer and heterodimer, 3 and 1 km mol⁻¹, yet its sum with its cross terms accounts for 85 km mol⁻¹ of the total intensity increase on complexation.

The bridge hydrogen atom contribution to the intensity increase, 574 km mol⁻¹, can account for almost all of the HF stretching intensity enhancement. The individual bridge hydrogen atom CCFDF contributions to the heterodimer HF intensity are very similar to the total values. Besides the 668 km mol⁻¹ bridge hydrogen contribution to the heterodimer HF stretching intensity, there are smaller contributions of 55 km mol⁻¹ from the donor hydrogen and fluorine atom cross term and -11 km mol⁻¹ from the two cross terms between the hydrogen of the HF donor molecule and the free water hydrogen atoms. All the contributions from the other atoms and two atom interactions are negligible.

CONCLUSIONS

Although the QAIM/CCFDF findings here confirm the importance of charge flux to the intensity enhancements of the H-bonded stretching of the water dimer found previously,⁹ an increase in the contribution owing to equilibrium charge displacement is found to be even more important. For the complexes treated here, decreases in charge flux on complex formation result in intensity enhancements because of the intensity contributions from interaction cross terms. For the symmetric and *antisymmetric* stretching modes of the water donor unit of the dimer the dipole flux interaction terms with charge and charge flux provide important contributions to the total intensities since the charge-charge flux interaction efficiently cancels the individual charge and charge flux contributions. The QAIM model results suggest that the infrared intensities of the water and HF dimers and their heterodimer are indeed very complex functions of these electronic structure parameters. On the other hand, these complex electronic structure changes owing only to the bridge hydrogen can be used to predict those intensity enhancements of the stretching vibrations of these three complexes.

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