

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/264381877>

Quantum Theory of Atoms in Molecules/Charge-Charge Flux-Dipole Flux Interpretation of fundamental vibrational intensity enhancements on H-bond formation of water trimer.

ARTICLE *in* CHEMICAL PHYSICS LETTERS · AUGUST 2014

Impact Factor: 1.9 · DOI: 10.1016/j.cplett.2014.07.002

READS

40

3 AUTHORS:



Arnaldo F. Silva

University of Campinas

11 PUBLICATIONS 20 CITATIONS

SEE PROFILE



Wagner E Richter

University of Campinas

12 PUBLICATIONS 20 CITATIONS

SEE PROFILE

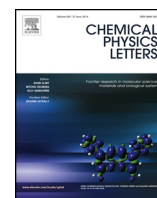


Roy E. Bruns

University of Campinas

256 PUBLICATIONS 3,243 CITATIONS

SEE PROFILE



Quantum Theory of Atoms in Molecules/Charge–Charge Flux–Dipole Flux interpretation of fundamental vibrational intensity enhancements on H-bond formation of water trimer



Arnaldo F. Silva, Wagner E. Richter, Roy E. Bruns*

Instituto de Química, Universidade Estadual de Campinas, CP 6154, Campinas, CEP 13.083-970 SP, Brazil

ARTICLE INFO

Article history:

Received 16 May 2014

In final form 1 July 2014

Available online 8 July 2014

ABSTRACT

The Quantum Theory Atoms in Molecules/Charge–Charge Flux–Dipole Flux model was used to investigate electronic structure variations associated with intensity changes for water trimer vibrations. The total of 440 km mol^{-1} experimental intensity for the symmetric stretches amounts to an average contribution of 147 km mol^{-1} per hydrogen bond. The calculated QCISD/cc-pVTZ value is 274 km mol^{-1} . The largest changes on complex formation occur for the charge, charge flux and their interaction. The hydrogen-bonded hydrogen atoms account for 99% of the total intensity of the two strongest symmetric stretches, mostly owing to mechanical vibration factors.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Through hydrogen bond formation some of the most dramatic changes in chemical properties occur. Among them, alterations in infrared spectra, such as frequency shifts and huge intensity enhancements of the H–X stretching vibrations are especially notable in simple and biologically relevant molecules [1–4]. Since these changes are very pronounced the absorption intensity of a vibrational band is often used as a probe of the hydrogen bond. Furthermore it has been suggested that a direct proportionality exists between hydrogen bonding energy and the intensifications of the $\nu_{(\text{H} \dots \text{X})}$ stretching vibration [5].

In order to extract quantitative information regarding the electronic structure of a molecule from its infrared spectrum one must first choose an adequate model. Relatively few research groups have invested their efforts in attempts to develop models to access information about this dramatic intensity enhancing effect. In this regard the literature includes partition procedures from studies of the Charge–Charge Flux–Overlap (CCFO) [6,7], Equilibrium Charge–Charge Flux (ECCF) [8–10] and Charge–Charge Flux–Dipole Flux (CCFDF) [11–13] models. Studies with much larger clusters (up to 30 molecules) focused on intra-intermolecular charge fluxes [14,15] and DFT methods have been used yielding results that are comparable with liquid water.

Of the infrared intensity enhancements on hydrogen bond formation, no instance is more dramatic than the symmetric stretch of the water dimer. The intensity increases from around 3 km mol^{-1} for the monomer [16] to 140 km mol^{-1} for the dimer [17]. Among others [10] our research group has invested efforts into studying this phenomenon. These studies take different approaches in order to explain the intensity enhancements in hydrogen bond complexes even though they agree that the main effect involves changes in charge transfers caused by the complex formation [18].

Developments in IR spectroscopic determinations involving encapsulation of small clusters in helium droplets [19] at very low temperatures reduced significantly errors involving spectral broadening, allowing intensity measurements of some molecular complexes. However uncertainties related to the size of the helium droplet [20] continues to result in much larger errors than usually found for simple gas phase determinations. Even so, this technique coupled with laser spectroscopy allowed the determination of some fundamental intensities of $(\text{H}_2\text{O})_n$, $n = 1, 2, 3$ and 4, in helium droplets [17,21] and enabling direct comparisons with the monomer. Neither experimental nor theoretical data for the water trimer are very abundant in literature, as most of the interest is focused on the dimer, where the intensity enhancement was first noticed. Nonetheless frequencies [22,23] and structural parameters [24] have been available in the literature for some time, and are useful to test the consistency of calculations as well as to characterize the normal coordinates of the water trimer.

In this work, the infrared enhancing effect observed for the water trimer is investigated at the QCISD level with a correlation consistent Dunning basis set using the Quantum Theory of

* Corresponding author.

E-mail address: bruns@iqm.unicamp.br (R.E. Bruns).

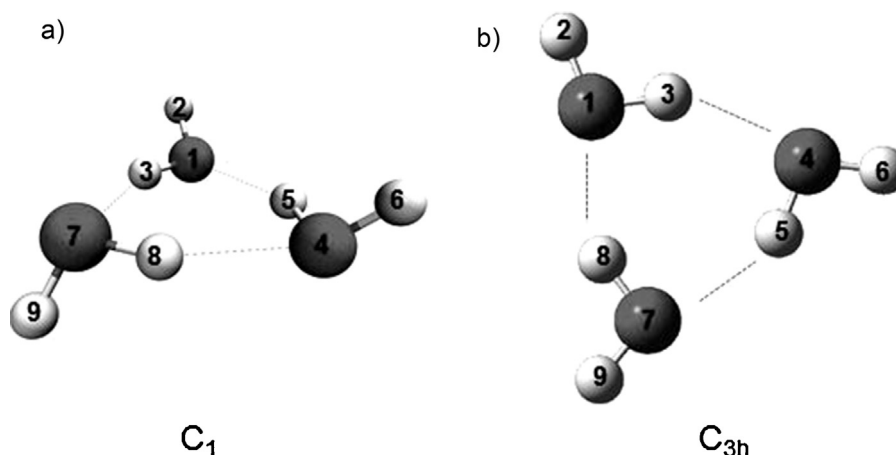


Fig. 1. (a) Optimized geometry and (b) C_{3h} approximate geometry for the water trimer.

Atoms in Molecules [25,26] (QTAIM)/Charge–Charge Flux–Dipole Flux [11,12] (CCFDF) model. The conclusions obtained in one of our previous works for the water dimer are expected to hold for the trimer, as this water cluster has similar normal coordinates, and the QCISD/cc-pVTZ level provides excellent estimates for the infrared intensities for both the monomer and the dimer.

2. Calculations

The experimentally proposed most stable [27] geometry for the water trimer does not exhibit molecular symmetry (*i.e.* C_1) and consists of three water molecules cyclically bonded with the free hydrogen atoms angled above and below the plan defined by the oxygen atoms. Another often-used approximate geometry consists of a C_{3h} planar complex. The torsion barrier of the free water trimer is rather low [28] (ranging from 0 to 20 kJ mol^{−1}) [29] making this C_{3h} geometry a useful approximation and hence simplifying analysis. Both geometries were used in this work and are presented in Figure 1.

Electronic structure calculations were carried out with GAUSSIAN03 [30] on an AMD 64 Opteron workstation. The geometries of both the most stable and the C_{3h} complex were optimized at the QCISD level with cc-pVTZ basis sets parting from experimental parameters [24]. The wave functions obtained were used in the subsequent QTAIM/CCFDF calculations. The infrared fundamental intensities were obtained at the same level described above. The MORPHY98 [31] program provided the QTAIM atomic charges and dipoles. These atomic quantities were used then by the PLACZEK [32,33] program to calculate the molecular dipole moment derivatives, and their charge, charge flux and dipole flux contributions as well.

3. Results

3.1. CCFDF contributions to the intensities

Table 1 contains the experimental values of the fundamental and infrared intensities for the water monomer and its (H₂O)_n, $n=2$ and 3 clusters as well as the intensities calculated using the QCISD/cc-pVTZ approach. The agreement between the theoretical and experimental intensities for the monomer [16] and dimer [17] is excellent especially upon considering the experimental errors. However there is a large discrepancy between the calculated and experimental intensities for the trimer. The *ab initio* calculation (822 km mol^{−1}) for the three symmetric stretching vibrations overestimate the available experimental infrared intensity [21]

(440 km mol^{−1}) by nearly a factor of 2. The experimentally measured intensity is the sum of the two nearly degenerate intense symmetric stretching bands, comparable with the sum of all the symmetric stretches calculated for the trimer. However, it is relevant to point out that the intensity measured experimentally for the trimer has an associated error of 30%, owing to the complicated analysis of co-existing monomer, dimer, trimer and even tetramer species in the infrared spectrum and droplet size distribution. Other theoretical calculations reported in literature from DFT (1100 km mol^{−1}) [34] and MP2 (950 km mol^{−1}, 920 km mol^{−1}) [35,36] even overestimate the experimental intensities by larger amounts.

Table 2 contains the QTAIM/CCFDF contributions for the monomer, dimer and trimer for the three corresponding fundamental bands of the water molecule as obtained in QCISD/cc-pVTZ calculations. Notice that each additional water molecule in a cluster yields 3 new high frequency normal coordinates (symmetric and asymmetric stretches and angular bending). The total intensities calculated from these CCFDF contributions are a little different from those obtained directly from the wave function due to errors in the numerical integration of the QTAIM parameters.

The normal coordinates for the symmetric stretches in Table 2 are shown in Figure 2. Two of these vibrations have one H-bonded O–H bond stretching with an opposite phase to the stretching of another H-bonded OH bond whereas the third one is relatively immobile. These two normal coordinates have the strongest absorptions, *i.e.* enhancement effects, with QCISD/cc-pVTZ intensities of 397 and 421 km mol^{−1}. The remaining stretching band consists of the three water units vibrating with the same phase, and its calculated intensity is only 4 km mol^{−1} due to the high symmetry of the normal coordinate. Calculations run with C_{3h} geometry confirmed this resulting in two strong (about 400 km mol^{−1}) doubly degenerate bands (E) that correspond to the two higher frequencies for the C_1 geometry. The lower frequency symmetric stretch calculated at the C_1 geometry becomes inactive with C_{3h} geometry as it is a totally symmetric normal coordinate (A_1).

The values presented for the water monomer and dimer were obtained and discussed in a previous work [13]. There is an enhancement in the experimental intensities of about 296 km mol^{−1} in the trimer above the 144 km mol^{−1} experimental value for the dimer. The 440 km mol^{−1} experimental intensity amounts to an average contribution of 147 km mol^{−1} per hydrogen bond close to the dimer value. However the calculated QCISD/cc-pVTZ enhancements for the symmetric stretches of the trimer sum to 822 or 274 km mol^{−1} per hydrogen bond.

Table 1

Vibrational data calculated for the water monomer and its clusters. The experimental values are also shown when available.

	Monomer				Exp.	
	Frequencies (cm ⁻¹)		Intensities (km mol ⁻¹)			
δ	1678		65.5		62.9 ± 7.5	
$\nu(\text{sym.})$	3872		4.3		2.7 ± 0.4	
$\nu'(\text{asym.})$	3975		42.4		43.2 ± 1.5	
	Dimer (PD) ^b		Dimer (PA) ^c		Exp.	
	Frequencies (cm ⁻¹)		Intensities (km mol ⁻¹)			
δ	1700	1676	48.0	73.9	–	–
$\nu(\text{sym.})$	3830	3874	162.5	8.7	144.0	4.5
$\nu'(\text{asym.})$	3954	3973	88.8	64.4	96.0	44.0
	<i>A'</i> ^a	<i>E'</i> ^a	<i>E'</i> ^a	<i>A'</i> ^a	<i>E'</i> ^a	Exp.
	Frequencies (cm ⁻¹)		Intensities (km mol ⁻¹)			
δ	1693	1698	1715	49.4	94.6	22.0
$\nu(\text{sym.})$	3681	3741	3745	4.4	420.8	397.0
$\nu'(\text{asym.})$	3937	3941	3942	89.1	83.4	53.4

^a Approximated geometry symmetry species C_{3h}.^b Proton donor.^c Proton acceptor.

As observed in our previous study for the dimer, the largest changes on trimer formation occur in the charge, charge flux and their interaction as seen in Table 2. The latter terms are always negative because the charge and charge flux contributions to the dipole moment derivatives have opposite signs. Note that the sum of the charge, charge flux and their interaction term ($C^2 + CF^2 + 2C \times CF$) for the symmetric stretch of the monomer and the asymmetric stretches of the monomer, dimer and trimer all have very small

values ranging from 4 to 18 km mol⁻¹ as can be seen in Table 2. On the other hand this sum for the dimer is 73 km mol⁻¹ and 216 and 241 km mol⁻¹ for the two strong bands of the trimer. These intensity increases stem from increases in equilibrium charges and decreases in vibrational charge transfer on hydrogen bond formation. These decreases have been previously reported by Popelier [37] as a clear consequence of the complex formation through hydrogen bonding, as the magnitude of dipolar polarization over

Table 2

Charge, charge-flux dipole-flux contributions for the symmetric stretches of the trimer, compared with the monomer and dimer.

	Monomer	Dimer	Trimer (3681 cm ⁻¹)	Trimer (3741 cm ⁻¹)	Trimer (3745 cm ⁻¹)
Symmetric stretch					
Charge (C)	251.9	336.1	6.4	611.5	590.7
Charge flux (CF)	360	179.1	12.4	158.9	127.4
Dipole flux (DF)	24.7	26.9	0.5	30.2	29.2
2C × CF	–602.3	–442.5	–0.1	–554.5	–477.2
2C × DF	158	187.3	3.1	259.2	244.8
2CF × DF	–188.8	–134.4	2.6	–112.5	–88.2
C + CF + 2C × CF	9.6	72.7	18.7	215.9	240.9
DF + 2C × DF + 2CF × DF	–6.1	79.8	6.2	176.9	185.8
Total intensity	3.5	152.5	24.8	392.8	426.8
	Monomer	Dimer	Trimer (3937 cm ⁻¹)	Trimer (3941 cm ⁻¹)	Trimer (3942 cm ⁻¹)
Asymmetric stretch					
Charge (C)	477.6	434.2	496.1	345.8	428
Charge flux (CF)	562.8	424.9	449.5	277.4	448.2
Dipole flux (DF)	68	60	66.1	43.9	54.6
2C × CF	–1036.9	–841.1	–928.6	–607.5	–867.3
2C × DF	360.5	322.1	361.4	246	305.6
2CF × DF	–391.3	–316.3	–342	–218.9	–310.8
C + CF + 2C × CF	3.5	18.0	17.0	15.7	8.9
DF + 2C × DF + 2CF × DF	37.2	65.8	85.5	71.0	49.4
Total intensity	40.7	83.8	102.5	86.8	58.3
	Monomer	Dimer	Trimer (1693 cm ⁻¹)	Trimer (1698 cm ⁻¹)	Trimer (1715 cm ⁻¹)
Angular bending					
Charge (C)	486.0	477.9	470.9	980	250.6
Charge flux (CF)	44.5	37	34.3	63.6	19.3
Dipole flux (DF)	52.2	78.3	76.3	183.5	43.8
2C × CF	–294.2	–266.1	–252	–497.3	–139.1
2C × DF	–318.5	–385.7	–378.5	–846.5	–209.2
2CF × DF	96.4	107.3	100.8	214.1	58.0
C ² + CF ² + 2C × CF	236.3	248.8	253.2	546.3	130.8
DF ² + 2C × DF + 2CF × DF	–169.9	–200.1	–201.4	–448.9	–107.4
Total intensity	66.4	48.7	51.8	97.3	23.5

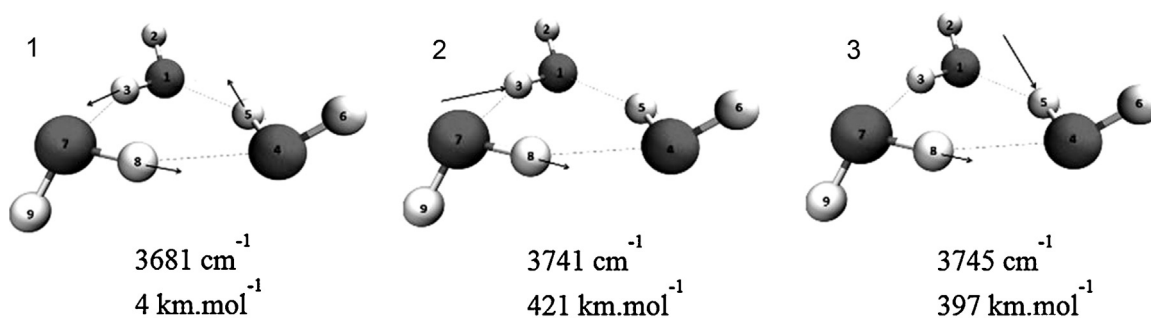


Fig. 2. Normal coordinates for the three symmetric stretches of the water trimer, labeled as 1 2 and 3.

the hydrogen atom diminishes. Furthermore they result in less negative charge flux – dipole flux terms so the net sum of this interaction with the dipole flux and charge-dipole flux interaction ($DF^2 + 2C \times DF + 2CF \times DF$) also results in substantial intensity increases. For the asymmetric stretches the charge contribution on complexation stays about the same and the decreases in charge transfer are more moderate. This results in small $C^2 + CF^2 + 2C \times CF$ sums and relative constant and moderate $DF^2 + 2C \times DF + 2CF \times DF$ sums for water monomer and complexes.

3.2. Atomic contributions to the intensities

In a previous work our group proposed the decomposition of the total dipole moment derivative with respect to the k th normal coordinate into atomic contributions [13]. Table 3 contains the atomic contributions and the total intensities of the three symmetric stretches of the water trimer. The most important contributions to the total intensity are from the hydrogen atoms involved in hydrogen bonding (“3”, “5” and “8”) and their interactions. The atomic contributions of the hydrogen atoms are always positive whereas their interactions can add or subtract intensity depending on their relative displacements. In fact almost all the intensity of these normal coordinates can be explained by the hydrogen atoms involved in hydrogen bonding, and their interactions, as they account for 421 and 388 km mol^{-1} for the higher frequency bands, compared with total QTAIM/CCFDF values of 427 and 393 km mol^{-1} . The remaining vibration is the lowest frequency symmetric stretch of the trimer that has quite a small predicted absorption intensity. Again the most important terms that contribute for the total intensity are the ones related

to the hydrogen atoms involved in hydrogen bonding (“3”, “5” and “8”). However in the last case, all the intensity added by the sum of the atomic contributions, $H(3) + H(5) + H(8)$, 282 km mol^{-1} is canceled by the interactions $H(3)H(5) + H(3)H(8) + H(5)H(8)$, -260 km mol^{-1} , resulting in 22 km mol^{-1} which is in pretty close agreement with the intensity obtained by the QTAIM/CCFDF result of 25 km mol^{-1} .

Taking a closer look at the atomic contributions for the 3741 cm^{-1} band, hydrogen atom “3” contributes with most of the intensity by a large margin (about 189 km mol^{-1}). The second largest contribution belongs to hydrogen “8”, with half of the amount attributed to hydrogen “3”. Hydrogen “5” barely provides any intensity (12 km mol^{-1}). As can be seen in Figure 2 these atomic contributions correlate with the relative lengths of the atomic displacements of the normal coordinate. A similar pattern is observed for the 3745 cm^{-1} intensity with largest contributions coming from hydrogen (5) followed by (8) and a very small value for hydrogen (3). Again the sizes of the atomic displacements and the atomic contributions in this normal coordinate show the same trend. The three hydrogen’s in the 3681 cm^{-1} symmetric stretch have somewhat more similar and moderate contributions. For this normal mode the three atomic displacements are about the same.

The factors causing the values of the atomic intensity contributions can be more completely understood by further examining their individual Charge–Charge Flux–Dipole Flux contributions. The dipole flux terms do not change significantly from the monomer to the dimer and trimer, and they are the least important contributions to the intensity enhancements for these vibrations. The charge and charge-flux contributions to the dipole moment

Table 3

Atomic contributions for the three different symmetric stretches for the water trimer and the sum of the mechanical weight defined in the text.

	3681 cm^{-1}		3741 cm^{-1}		3745 cm^{-1}	
	Mech. weigh	Intensity	Mech. weigh	Intensity	Mech. weigh	Intensity
O(1)	0.001	0.5	0.002	0.8	0.000	0.0
H(2)	0.016	0.5	0.032	1.0	0.000	0.0
H(3)	0.342	121.4	0.526	188.7	0.027	9.5
O(4)	0.001	0.3	0.000	0.0	0.002	0.6
H(5)	0.237	63	0.045	12.3	0.607	163.4
H(6)	0.012	0.4	0.006	0.2	0.037	1.3
O(7)	0.001	0.5	0.001	0.4	0.001	0.3
H(8)	0.318	97.1	0.320	98.2	0.255	78.4
H(9)	0.016	0.8	0.015	0.7	0.019	0.9
H(3)H(5)	−0.149	−85.2	0.080	46.4	0.065	37.8
H(3)H(8)	−0.164	−71.2	0.202	89	−0.042	−18.3
H(5)H(8)	−0.131	−103.7	−0.059	−46.6	0.187	149.9
Other	–	0.5	–	1.6	–	2.9
Total	–	24.8	–	392.8	–	426.8

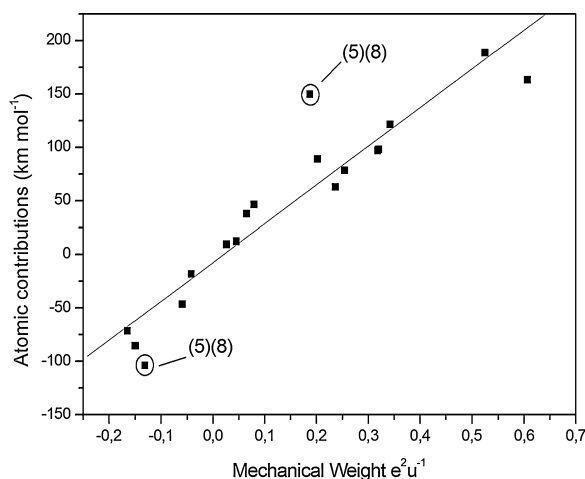


Fig. 3. Atomic Contributions vs. sum of the mechanical weight defined in the text for the hydrogen atoms involved in the hydrogen bond for the water trimer.

derivatives however are responsible for the intensity enhancement observed for both the dimer and trimer, and can be express as:

$$\left(\frac{\partial p_{\sigma}}{\partial Q_k}\right)_{C(i)} = q_i \left(\frac{\partial \sigma_i}{\partial Q_k}\right) \quad \text{and} \quad \left(\frac{\partial p_{\sigma}}{\partial Q_k}\right)_{CF} = \sum_j^{3N} \left[\sum_i^N \left(\frac{\partial q_i}{\partial \sigma_j}\right) \sigma_i \right] \left(\frac{\partial \sigma_j}{\partial Q_k}\right)$$

where $\sigma = x, y$ or z for the i th atom. Both charge and charge flux terms contain an electronic (charge and charge derivative) and a mechanical (Cartesian/normal coordinate derivative) factor.

Since the atomic charges and charge fluxes of the three hydrogen atoms are very similar one would expect that the large differences between their atomic contributions are not due to electronic factors. Thus the reason that the hydrogen atoms contribute with different parcels to the total intensities must be related to mechanical factors, *i.e.* their relative displacements for the normal coordinates. Therefore if the displacement amplitude of an atom in the vibration is large, its contribution should be very relevant to the total infrared intensity. Furthermore the sign of the atomic interaction between two atoms will be determined by their relative motion in the normal coordinate. When two atoms move in the same direction their interaction will reinforce the intensity, while if they move in opposite directions the intensity is decreased.

Since the atomic normal coordinate possesses x, y and z components the total weight of the mechanical parcel is $\sum_{\sigma=x,y,z} (\partial \sigma_i / \partial Q_k)^2$ for an atomic contribution and $\sum_{\sigma=x,y,z} (\partial \sigma_i / \partial Q_k) (\partial \sigma_j / \partial Q_k)$ for an interaction. Figure 3 graphs the mechanical weights of the hydrogen atoms participating in the hydrogen bonds of these normal coordinates vs. their respective atomic contribution or interaction. One can see that there is a linear tendency between these two quantities that has a correlation coefficient of 0.93 showing the importance of the mechanical

factors in determining the atomic contributions as well as the total intensities of the symmetric H-bond stretching vibrations.

Acknowledgements

W.E.R. and A.F.S. thank CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) for graduate student fellowships (grants 140916/2011-3 and 140711/2013-9) and R.E.B. thanks CNPq for a research fellowship. We are also grateful to FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo) for partial financial support of this work (grants 2010/18743-1 and 2009/09678-1).

References

- [1] G.C. Pimentel, A.L. McClellan, *The Hydrogen Bond*, W.H. Freeman and Co, San Francisco, 1960.
- [2] C.M. Huggins, G.C. Pimentel, *J. Phys. Chem.* 60 (12) (1956) 1615.
- [3] A.G. Ponomareva, Y.P. Yurenko, R.O. Zhuravitsky, T. Mourik, D.M. Hovorun, *Phys. Chem. Chem. Phys.* 14 (2012) 6787.
- [4] T.Y. Nikolaenko, L.A. Bulavin, D.M. Hovorun, *Phys. Chem. Chem. Phys.* 14 (2012) 7441.
- [5] A.V. logansen, *Spectrochim. Acta A* 55 (1999) 1585.
- [6] W.T. King, G.B. Mast, *J. Phys. Chem.* 80 (1979) 2521.
- [7] B.A. Zilles, W.A. Person, *J. Chem. Phys.* 79 (1983) 65.
- [8] J.C. Decius, *J. Mol. Spectrosc.* 57 (1975) 348.
- [9] M. Gussoni, P. Jona, G. Zerbi, *J. Chem. Phys.* 78 (1983) 6802.
- [10] D. Galimberti, A. Milani, C. Castiglioni, *J. Chem. Phys.* 138 (2013) 164115; D. Galimberti, A. Milani, C. Castiglioni, *J. Chem. Phys.* 139 (2013) 074304.
- [11] R.L.A. Haiduke, R.E. Bruns, *J. Phys. Chem. A* 109 (2005) 2680.
- [12] A.F. Silva, W.E. Richter, H.G.C. Meneses, S.H.D.M. Faria, R.E. Bruns, *J. Phys. Chem. A* 116 (2012) 8238.
- [13] A.F. Silva, W.E. Richter, L.A. Terrabuio, R.L.A. Haiduke, R.E. Bruns, *J. Chem. Phys.* 140 (2014) 8436.
- [14] H. Torii, *J. Phys. Chem. B* 114 (2010) 13403.
- [15] H. Torii, *J. Phys. Chem. A* 114 (2013) 2044.
- [16] F. Culot, J. Likvin, *Phys. Scr.* 46 (1992) 502.
- [17] K. Kuyanov-Prozument, M.Y. Choi, A.F. Vilesov, *J. Chem. Phys.* 132 (2010) 14304.
- [18] A.M. Pendás, M.A. Blanco, E. Francisco, *J. Chem. Phys.* 125 (2006) 184112.
- [19] M. Hartmann, R.E. Miller, J.P. Toennies, A. Vilesov, *Phys. Rev. Lett.* 75 (1995) 1566.
- [20] M. Leweretz, B. Schilling, J.P. Toennies, *J. Chem. Phys.* 102 (1995) 8191.
- [21] M.N. Slipchenko, K.E. Kuyanov, B.G. Sartakov, A.F. Vilesov, *J. Chem. Phys.* 124 (2006) 241101.
- [22] R.M. Bentwood, A.J. Barnes, W.J. Orville-Thomas, *J. Mol. Spectrosc.* 84 (1980) 391.
- [23] A. Engdahl, B. Nelander, *J. Chem. Phys.* 86 (1987) 4831.
- [24] E.S. Campbell, M. Mezei, *J. Chem. Phys.* 67 (1985) 2338.
- [25] R.F.W. Bader, A. Larouche, C. Gatti, M.T. Carrol, P.J. MacDougall, K.B. Wiberg, *J. Chem. Phys.* 87 (1987) 1142.
- [26] R.F.W. Bader, *Atoms in Molecules: A Quantum Theory*, Clarendon Press, Oxford, 1990.
- [27] B. Tremblay, B. Madebène, M.E. Alikhani, J.P. Perchard, *Chem. Phys.* 378 (2010) 27.
- [28] J. Ceponkus, G. Karlström, B. Nelander, *J. Phys. Chem. A* 109 (2005) 7859.
- [29] D.J. Wales, *J. Am. Chem. Soc.* 115 (1993) 11180.
- [30] M.J. Frisch, et al., *GAUSSIAN03, Revision D.02*, Gaussian Inc., Wallingford, CT, 2004.
- [31] MORPHY98, a program written by P.L.A. Popelier with a contribution from R.G.A. Bone, UMIST, Manchester, England, EU 1998.
- [32] L.N. Vidal, P.A.M. Vazquez, *Quim. Nova* 26 (4) (2003) 507.
- [33] L.N. Vidal, P.A.M. Vazquez, *Int. J. Quantum Chem.* 103 (5) (2005) 632.
- [34] K. Ohno, M. Okimura, N. Akai, Y. Katsumoto, *Phys. Chem. Chem. Phys.* (2005) 3005.
- [35] S.S. Xantheas, T.H. Dunning Jr., *J. Chem. Phys.* 99 (1993) 8774.
- [36] G.M. Chaban, J.O. Jung, R.B. Gerber, *J. Phys. Chem.* 104 (2000) 2772.
- [37] U. Koch, P.L.A. Popelier, *J. Phys. Chem.* 99 (1995) 9747.