

Rayleigh light scattering of hydrogen bonded clusters investigated by means of *ab initio* calculations

Eudes E Fileti, Roberto Rivelino and Sylvio Canuto¹

Instituto de Física, Universidade de São Paulo, CP 66318, 05315-970 São Paulo, SP, Brazil

E-mail: canuto@if.usp.br

Received 21 September 2002, in final form 9 December 2002

Published 13 January 2003

Online at stacks.iop.org/JPhysB/36/399

Abstract

Ab initio calculations of depolarization ratios and intensities of classically scattered light, in terms of dipole polarizabilities and polarizability anisotropies, are reported for different hydrogen bonded molecular clusters. Five different groups of organic heterodimers formed with water are considered: $\text{HCHO} \cdots \text{H}_2\text{O}$, $\text{CH}_3\text{HO} \cdots \text{H}_2\text{O}$, $\text{HCOOH} \cdots \text{H}_2\text{O}$, $\text{CH}_3\text{CN} \cdots \text{H}_2\text{O}$, and $(\text{CH}_3)_2\text{CO} \cdots \text{H}_2\text{O}$, together with the water dimer $\text{H}_2\text{O} \cdots \text{H}_2\text{O}$. The geometries of all complexes have been optimized by means of the second-order Møller–Plesset many-body perturbation theory (MP2), using the augmented correlation-consistent basis set with polarized valence of double-zeta quality (aug-cc-pVDZ). The calculated average dipole polarizabilities of the isolated molecules are in good agreement with available experimental results. The calculations are then extended to the complexes and, from these, the Rayleigh scattering activities and depolarization ratio changes, upon hydrogen bond formation, are obtained and analysed. The differences in activity and depolarization for Rayleigh scattered radiation between two groups of isomers, (i) $\text{HCN} \cdots \text{H}_2\text{O}$ and $\text{H}_2\text{O} \cdots \text{HCN}$ and (ii) $\text{CH}_3\text{HO} \cdots \text{H}_2\text{O}$ and $\text{CH}_3\text{OH} \cdots \text{OH}_2$, have also been investigated.

1. Introduction

The molecular scattering of light provides a great spread of information about the finest details of phenomena observed in the interaction of radiation with matter [1, 2]. The basic descriptor of the interaction of the molecular charge distribution with an electric field is the dipole polarizability [3], which is also connected with the partial orientation of anisotropic pairs [4]. Electromagnetic radiation can scatter off molecules in two well-understood processes: one is elastic or Rayleigh scattering and the other is inelastic scattering, better known as Raman scattering, in which the wavelength of the radiation is degraded in the process. The elastic

¹ Author to whom any correspondence should be addressed.

scattering of light is primarily a classical effect caused by optical inhomogeneities in the medium or time fluctuations in its optical density. In this sense, by examining the state of polarization of the incident light beam of the system under study, it is possible to find the degree of depolarization of each frequency shift in the light scattering spectrum, a quantity that is important in the interpretation of the experimental results. This quantity is the ratio, for the scattered light, of the intensities of the components polarized perpendicular and parallel, respectively, to the direction of polarization of the incident beam. In such a description, the state of polarization of the scattered light is related to the molecular anisotropy [2]. Hence, for molecules, the Rayleigh scattering properties are connected with both the dipole polarizability and the polarizability anisotropy [5].

Rayleigh scattering investigation has been used as a successful technique for obtaining the average size of clusters formed in molecular beams under different expansion conditions [6–8]. The depolarized component of the Rayleigh scattered radiation has also been used to obtain molecular species concentrations in plasmas [9], because the scattering signal is related to the number of scattering particles in the medium [6, 7]. Recently, Park *et al* [10] have proposed that the internal hydrogen bonding strength changes in *cis-trans* photoisomerization processes can be monitored by forced Rayleigh scattering. Also, dynamical aspects of hydrogen bond formation in aqueous solutions can be studied by means of depolarized Rayleigh light scattering (DRLS). Along this lines, Micali *et al* [11] have investigated the water rotational relaxation time in water–methanol solutions as a function of concentration and temperature. Thus, molecular light scattering spectra can give information on both microscopic and collective properties of the scatterer centres. From the structural point of view, asymmetrical molecules are well known to give a strong contribution to the depolarized Rayleigh intensity, so DRLS can be used to study molecular rotational dynamics [11] or even the strength of the bond energy for assembled molecules [1]. More generally, the phenomenon of molecular scattering of light can be studied in gases or vapours, liquids, and crystals [2].

In this work we determine depolarization ratios and activities for Rayleigh light scattering in terms of *ab initio* polarizabilities of hydrogen bonded molecular clusters. The formation of hydrogen bonds is expected to lead to an increase in the polarizability anisotropy and therefore a change in the Rayleigh depolarization ratio. The systems studied here are different types of hydrogen bonded complexes formed with water, for instance $\text{H}_2\text{O} \cdots \text{H}_2\text{O}$, $\text{HCHO} \cdots \text{H}_2\text{O}$, $\text{CH}_3\text{HO} \cdots \text{H}_2\text{O}$, $\text{HCOOH} \cdots \text{H}_2\text{O}$, $\text{CH}_3\text{CN} \cdots \text{H}_2\text{O}$, and $(\text{CH}_3)_2\text{CO} \cdots \text{H}_2\text{O}$. The water dimer has been extensively [12–21] studied before, but studies of other hydrogen bonded systems are more scarce and, in particular, the characterization of alcohol–water systems is of great importance [11]. The electronic changes upon hydrogen bond formation can be probed by a great variety of techniques such as infrared spectroscopy, rotational millimetre spectroscopy, nuclear magnetic resonance, Raman spectroscopy, and depolarization studies. However, very little time has been dedicated to the Rayleigh scattering techniques used in hydrogen bonded systems. One possible reason for this is the small magnitude of the changes expected. Another is that Rayleigh light scattering is related to dipole polarizability which is, in fact, the basic property that describes the interaction of a molecule with an electric field [22]. Because of the lack of both theoretical and experimental results on depolarization ratios of Rayleigh scattering for small hydrogen bonded clusters, this study might be of interest in establishing possible trends and predictions for classically scattered light in these systems. In addition, the difference in depolarization for Rayleigh scattered radiation between two groups of hydrogen bonded isomers, (i) $\text{HCN} \cdots \text{H}_2\text{O}$ and $\text{H}_2\text{O} \cdots \text{HCN}$ and (ii) $\text{CH}_3\text{HO} \cdots \text{H}_2\text{O}$ and $\text{CH}_3\text{OH} \cdots \text{OH}_2$, has also been investigated here. For these cases the water molecule acts as both proton donor and proton acceptor. Hence, the changes in the molecular depolarization light scattering spectra of the clusters are used to critically assess the depolarized Rayleigh

scattering as an additional possible mean of distinguishing among these intermolecular isomers. Furthermore, a study of the Rayleigh light scattering, such as that carried out here, could be a viable alternative method for possible identification and characterization of molecular segregation in alcohol–water mixtures [23].

2. Theory and methods

According to the formalism of classical scattering, in the case of non-spherically symmetric molecules a small component of the scattered radiation is depolarized at right angles to the direction of incidence [24, 25]. In depolarized Rayleigh scattering the scattered light is detected with a polarization perpendicular to that of the incident radiation, whereas the polarized Rayleigh spectrum detects light scattered with the same polarization direction as the incident light [5]. The quantities most frequently observed experimentally are the depolarization ratios (or degree of depolarization) for both natural and plane-polarized light, given, respectively, by

$$\sigma_n = \frac{6(\Delta\alpha)^2}{45(\bar{\alpha})^2 + 7(\Delta\alpha)^2}, \quad (1)$$

$$\sigma_p = \frac{3(\Delta\alpha)^2}{45(\bar{\alpha})^2 + 4(\Delta\alpha)^2}. \quad (2)$$

In equations (1) and (2), $\bar{\alpha} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$ is the average dipole polarizability and $(\Delta\alpha)^2 = \frac{1}{2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2] + 3[(\alpha_{xy})^2 + (\alpha_{xz})^2 + (\alpha_{yz})^2]$ is the polarizability anisotropy, where α_{ij} are the components of the polarizability tensor, α , along the molecular axis of the system.

The largest value of the degree of depolarization occurs for the most anisotropic case. Because $\bar{\alpha}$ always has a non-zero value for Rayleigh scattering, the maximum value of σ_n^{\max} is $\frac{1}{2}$, while the maximum value of σ_p^{\max} is $\frac{1}{3}$. For the sake of completeness, it is also of interest to obtain the depolarization for circularly polarized light. The scattered light, which is circularly polarized, may contain a component of circular polarization given by

$$\sigma_c = \frac{\sigma_n}{1 - \sigma_n}. \quad (3)$$

In this case the maximum value of the depolarization is $\sigma_c^{\max} = 1$. The Rayleigh scattered light intensity (or Rayleigh activity) can also be obtained in terms of polarizability for natural and plane-polarized light as follows:

$$\mathfrak{R}_n = 45(\bar{\alpha})^2 + 13(\Delta\alpha)^2, \quad (4)$$

$$\mathfrak{R}_{p\perp} = 45(\bar{\alpha})^2 + 7(\Delta\alpha)^2, \quad (5)$$

$$\mathfrak{R}_{p\parallel} = 6(\Delta\alpha)^2. \quad (6)$$

As usual [5, 24], the Rayleigh intensity associated with the plane-polarized light, \mathfrak{R}_p , has been split into two orthogonal parts: $\mathfrak{R}_{p\perp}$, which corresponds to light perpendicularly polarized into the scattering plane; and $\mathfrak{R}_{p\parallel}$, which corresponds to light polarized in the same plane of scattering.

The static polarizability tensor, α , is calculated here using the finite-field approximation [21, 26, 27], in which the total energy of the system is calculated both in the absence and in the presence of a weak electric field [28]. Thus, the electric properties are determined as derivatives of the energy with respect to the electric field. The components of the field strengths used here are 0.001 au. The *ab initio* calculations for the isolated molecules and their water complexes are performed by using the Møller–Plesset perturbation theory up to second order (MP2) [29]. This is carried out utilizing the augmented correlation-consistent

basis set with polarized valence of double-zeta quality (aug-cc-pVDZ) [30]. Thus, the full equilibrium geometries of the systems are found and the dipole polarizabilities are calculated with the MP2/aug-cc-pVDZ method. At this level of theory, the size extensivity is guaranteed. As all hydrogen bonded systems considered here involve the water molecule, it is important to mention that the MP2/aug-cc-pVDZ theoretical model gives a dipole moment of 1.88 D for this molecule, which is in very good agreement with the experimental value of 1.86 D [31]. Finally, the quantum mechanical calculations reported in this work were performed using the GAUSSIAN98 program [32].

3. Results and discussion

3.1. Dipole polarizabilities and polarizability anisotropies

The fully optimized structures of the clusters considered in this work are presented in figure 1, where the hydrogen bond lengths are shown. All these hydrogen bonded systems have been found to be stable complexes at different levels of theory. There have been several theoretical studies of the water dimer. Schütz *et al* [33] and Xantheas [34] have obtained an accurate value of 2.925 Å for the O–O interatomic distance. More recently, Maroulis [35] has obtained the value of 2.911 Å. These values are in good agreement with our calculated O–O distance of 2.918 Å. In the case of HCHO ··· H₂O, our calculated hydrogen bond distance of 1.986 Å is shorter by 0.075 Å than the result of Tsuzuki *et al* [36] obtained using MP2/6-311G(d, p). For CH₃HO ··· H₂O our calculated hydrogen bond distance (O ··· H) of 1.904 Å corresponds to an O–O distance of 2.844 Å, which compares well with the experimental result of 2.997 Å [37] and the recent theoretical result of 2.840 Å obtained using the MP2/aug-cc-pVDZ model [38]. For HCOOH ··· H₂O our calculated hydrogen bond distances of 2.040 and 1.817 Å compare well with the results of Wei *et al* [39] of 2.10 and 1.80 Å obtained using MP2/6-311 ++ G(2d, 2p). In the case of CH₃CN ··· H₂O, the distance of 2.059 Å can be compared with a previous result of 2.108 Å [40] obtained with another basis set using MP2/6-311 ++ G(d, p), and for (CH₃)₂CO ··· H₂O the distance of 1.914 Å compares well with our previous estimate [41] of 1.918 Å obtained using MP2/6-311 + G. The results presented here are all obtained using a single theoretical model, MP2/aug-cc-pVDZ, and serve better for comparison purposes among the different species.

In table 1 we report the calculated dipole polarizabilities and anisotropies of the isolated molecules, and their corresponding water clusters, obtained with the MP2/aug-cc-pVDZ method. Our results for the average polarizabilities of the isolated molecules are in fairly good agreement with the available experimental data [42]. For the water dimer, Maroulis [35] has calculated an average dipole polarizability of 19.5 au, in good agreement with our present result of 19.10 au. In some cases different experimental values have been reported. For instance, in the case of methanol (CH₃OH) our calculated result of 21.22 au is in good agreement with three reported values. In general, however, our calculated mean polarizabilities are slightly smaller than the experimental values but slightly larger than other reported theoretical results [43], as in the case of formic acid (HCOOH) and acetonitrile (CH₃CN). The agreement of the theoretical polarizability with the corresponding experimental values depends strongly on the quality of the basis set, as pointed out by Nakagawa [44] for methanol (CH₃OH). Additionally, we have evaluated the so-called interaction polarizability [35] upon complexation of each monomer with water. This is defined by $\bar{\alpha}_{\text{inter}} = \bar{\alpha}(\text{complex}) - [\bar{\alpha}(\text{H}_2\text{O}) + \bar{\alpha}(\text{monomer})]$. As observed by Maroulis [35], the basis set superposition error (BSSE) is quite small for this quantity at correlated levels. The calculated values of $\bar{\alpha}_{\text{inter}}$ for all complexes given in table 1 are very small, being less than 1.0 au in all cases. For instance, in the case of the water dimer we have

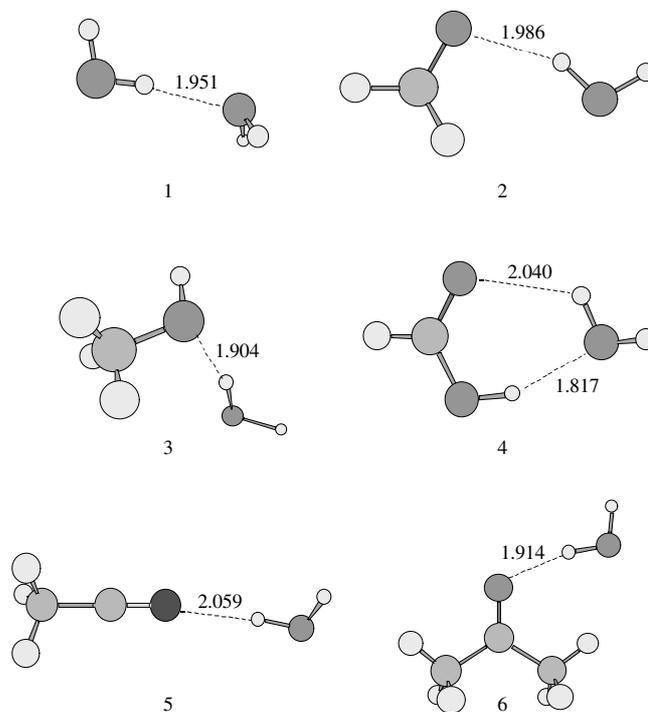


Figure 1. Structures of the hydrogen bonded water complexes: $\text{H}_2\text{O}\cdots\text{H}_2\text{O}$ (1), $\text{HCHO}\cdots\text{H}_2\text{O}$ (2), $\text{CH}_3\text{HO}\cdots\text{H}_2\text{O}$ (3), $\text{HCOOH}\cdots\text{H}_2\text{O}$ (4), $\text{CH}_3\text{CN}\cdots\text{H}_2\text{O}$ (5), and $(\text{CH}_3)_2\text{CO}\cdots\text{H}_2\text{O}$ (6). The lengths of the H bonds are given in Å, as obtained at the MP2/aug-cc-pVDZ level.

calculated such an interaction as having the value 0.5 au; the value found by Maroulis [35] was even smaller, at a very different level of calculation. Of course, a small value for $\bar{\alpha}_{\text{inter}}$ indicates that the dipole polarizability of the hydrogen bonded systems is approximately the sum of the separate parts. The largest deviation of $\bar{\alpha}_{\text{inter}}$ calculated here is for acetonitrile. As the polarizability anisotropies reflect the symmetry of the system, it is interesting to note their changes due to hydrogen bond formation. For instance, the anisotropies of the water dimer and $\text{CH}_3\text{HO}\cdots\text{H}_2\text{O}$ change equally, by 2.52 au. This value is only 1.74 au for $\text{HCHO}\cdots\text{H}_2\text{O}$ and 2.29 au for $\text{HCOOH}\cdots\text{H}_2\text{O}$, and increases to about 4.92 au for $(\text{CH}_3)_2\text{CO}\cdots\text{H}_2\text{O}$ and 6.13 au for $\text{CH}_3\text{CN}\cdots\text{H}_2\text{O}$. These different anisotropies will lead to different changes in the depolarization ratios.

3.2. Depolarization ratios and intensities for Rayleigh scattering

The quantities most commonly observed in light scattering experiments are the depolarization ratios [5], defined previously in equations (1), (2), and (3). The changes in the polarizability and anisotropy lead to variations in the depolarization ratios of the hydrogen bonded clusters. We have computed all the components of the depolarization due to natural, plane-polarized, and circularly polarized light incident on the isolated molecules and their corresponding water clusters, which are shown in figure 1. In table 2 we give the components of the depolarization ratios for each system as obtained at the MP2/aug-cc-pVDZ level. As normally expected, the increase in anisotropy should lead to an increase in the depolarization ratios. The opposite

Table 1. Calculated mean polarizabilities, interaction polarizabilities, and polarizability anisotropies (in au), at the MP2/aug-cc-pVDZ level. Conversion unit for dipole polarizability: 1 au = 0.148 Å³.

System	$\bar{\alpha}$	$\bar{\alpha}_{\text{inter}}$	$\Delta\alpha$	$\alpha_{\text{exp}}^{\text{a}}$	Other results for $\bar{\alpha}$
H ₂ O	9.30	—	1.04	9.80	9.78 [35]
H ₂ O...H ₂ O	19.10	0.50	3.56		19.5 [35]
HCHO	17.58	—	8.57	18.9, 16.55	17.83 [4]
HCHO...H ₂ O	27.01	0.13	10.31		
CH ₃ OH	21.22	—	3.38	22.21, 21.80, 22.41	21.6 [44]
CH ₃ HO...H ₂ O	31.19	0.67	5.90		
HCOOH	22.53	—	10.64	22.97	20.29 [43]
HCOOH...H ₂ O	32.15	0.32	12.93		
CH ₃ CN	29.43	—	15.65	29.72, 30.27	28.14 [43]
CH ₃ CN...H ₂ O	39.67	0.94	21.78		
(CH ₃) ₂ CO	42.38	—	12.38	43.24, 43.17, 42.77	43.30 [4]
(CH ₃) ₂ CO...H ₂ O	52.20	0.52	17.30		

^a Experimental polarizabilities are available only for the isolated molecules [42].

occurs, however, in the cases of formaldehyde (HCHO) and formic acid (HCOOH) upon complexation with water. In the first case, the variation in the depolarization of plane-polarized light (σ_p) is -38% upon binding the water molecule. Similarly, in the case of HCOOH this variation is -27% upon hydrogen bond formation. On the other hand, this variation increases to 18% for CH₃HO...H₂O, 22% for (CH₃)₂CO...H₂O, and only 6.4% for CH₃CN...H₂O. For the case of the water dimer, σ_p more than doubles, that is, increases from 0.17×10^{-2} to 0.46×10^{-2} . A similar behaviour is also observed for the natural and circularly polarized light, as shown in table 2. It is interesting to observe that all components of depolarization for the water dimer and CH₃HO...H₂O complex give essentially the same values. For instance, the depolarization ratio for circularly polarized light (σ_c) is computed as 0.46×10^{-2} for (H₂O)₂ and only 0.47×10^{-2} for CH₃HO...H₂O. These values are very close, because the basic difference between the two hydrogen bonded clusters, XOH...H₂O, is just the substituent group X = H or CH₃ in the geometric structure. Thus, it is difficult to distinguish between the two complexes just by using depolarized Rayleigh scattering. As we will discuss later, the two heterodimers of methanol and water give the same degree of depolarization as the water dimer. Complementary determinations of other properties are necessary to distinguish between the different complexes.

In table 3 we give the calculated Rayleigh intensities for the hydrogen bonded complexes for all of the components of light. The increase factors with respect to the isolated molecules are also given. For instance, the Rayleigh intensity for natural light in the case of the formaldehyde–water complex, $\mathfrak{R}_n(\text{HCHO} \cdots \text{H}_2\text{O})$, is calculated as 3.420×10^4 au. This represents a factor of 2.3 compared to the same intensity for the isolated HCHO formaldehyde molecule (calculated as 1.487×10^4 au). As can be seen, the formation of the hydrogen bond leads to a considerable increase in the Rayleigh intensity. As table 3 shows, this increase occurs for all polarizations. Typically the increase factor is close to 2.0, but in the case of the water dimer it is even larger. The variations of \mathfrak{R}_n and $\mathfrak{R}_{p\perp}$ reflect the strong dependence of the Rayleigh activity on the polarizability and the smaller contribution from the anisotropy. For isolated H₂O the intensity is calculated as 3.907×10^4 au, whereas for the smallest complex considered here, the dimer (H₂O)₂, it is 1.658×10^4 au, corresponding to an increase factor of 4.2 and an absolute increase of 1.267×10^4 au for natural light. For acetone–water, the largest complex considered here, the corresponding increase factor is 1.5 with an absolute increase

Table 2. Depolarization ratios for different types of incident light, calculated in terms of the polarizabilities and polarizability anisotropies. All values are obtained at the MP2/aug-cc-pVDZ level.

System	$\sigma_n (\times 10^{-2})$	$\sigma_p (\times 10^{-2})$	$\sigma_c (\times 10^{-2})$
H ₂ O	0.17	0.08	0.17
H ₂ O...H ₂ O	0.46	0.23	0.46
HCHO	3.05	1.55	3.15
HCHO...H ₂ O	1.90	0.96	1.94
CH ₃ OH	0.34	0.17	0.34
CH ₃ HO...H ₂ O	0.47	0.24	0.47
HCOOH	2.87	1.46	2.95
HCOOH...H ₂ O	2.10	1.06	2.14
CH ₃ CN	3.61	1.84	3.74
CH ₃ CN...H ₂ O	3.84	1.96	3.99
(CH ₃) ₂ CO	1.12	0.56	1.13
(CH ₃) ₂ CO...H ₂ O	1.44	0.72	1.46

Table 3. Rayleigh intensities (in 10⁴ au) calculated in terms of the polarizabilities and polarizability anisotropies. Values in parentheses correspond to the increase factor of the intensity upon complexation with water. All values are computed at the MP2/aug-cc-pVDZ level.

System	\mathfrak{R}_n	$\mathfrak{R}_{p\perp}$	$\mathfrak{R}_{p\parallel}$
H ₂ O...H ₂ O	1.658 (4.24)	1.650 (4.23)	0.008 (11.73)
HCHO...H ₂ O	3.420 (2.30)	3.357 (2.33)	0.064 (1.45)
CH ₃ HO...H ₂ O	4.424 (2.17)	4.403 (2.16)	0.021 (3.03)
HCOOH...H ₂ O	4.868 (2.00)	4.767 (2.02)	0.100 (1.47)
CH ₃ CN...H ₂ O	7.700 (1.83)	7.415 (1.82)	0.284 (1.94)
(CH ₃) ₂ CO...H ₂ O	12.652 (1.53)	12.472 (1.52)	0.180 (1.95)

of 4.372×10^4 au. The percentage increase presents an opposite behaviour to the size of the hydrogen bonded clusters. While the differences in Rayleigh light scattered intensities upon dimerization of water correspond to 76% of the total intensity of the dimer, the complex formation of acetone ((CH₃)₂CO) with water gives only 35%. Indeed, for the case of the water molecule, its polarizability becomes more than twice the original value for one molecule because of dimerization, whereas for acetone–water complexation, this increase amounts to only 23%. As regards $\mathfrak{R}_{p\parallel}$, this is given entirely by the anisotropic polarizability, $6(\Delta\alpha)^2$. The water dimer is the most anisotropic complex, thus giving a relative variation in $\mathfrak{R}_{p\parallel}$ of 92%, while HCHO...H₂O—and HCOOH...H₂O—give only 31% (32%).

3.3. Rayleigh light scattering of isomers

The spectroscopic characterization of intermolecular isomers can effectively be carried out using ro-vibrational spectroscopy techniques. Indeed, upon hydrogen bond complex formation, the stretching modes shift their vibrational frequencies towards the low-energy band. In this section we investigate the Rayleigh light scattering properties for two groups of hydrogen bonded isomers: (i) HCN...H₂O and H₂O...HCN and (ii) CH₃HO...H₂O and CH₃OH...OH₂, where the water molecule acts as both proton donor and proton acceptor.

The MP2/aug-cc-pVDZ optimized geometries of the two possible heterodimers, hydrogen cyanide–water and methanol–water, are given schematically in figure 2. In a previous work, we calculated the stability of the hydrogen cyanide–water isomers using CCSD(T)//MP2/6-

Table 4. Calculated mean polarizabilities and polarizability anisotropies (in au), and Rayleigh depolarization ratios. All values are computed at the MP2/aug-cc-pVDZ level.

Isomers	$\bar{\alpha}$	$\Delta\alpha$	$\sigma_n (\times 10^{-2})$	$\sigma_p (\times 10^{-2})$	$\sigma_c (\times 10^{-2})$
H ₂ O...HCN	26.74	13.74	3.38	1.72	3.49
HCN...H ₂ O	22.60	15.37	5.75	2.96	6.10
CH ₃ HO...H ₂ O	31.19	5.90	0.47	0.24	0.47
CH ₃ OH...OH ₂	30.67	5.25	0.40	0.20	0.40

Table 5. Rayleigh intensities (in 10⁴ au) calculated in terms of the polarizabilities and polarizability anisotropies. Values in parentheses correspond to the increase factor of the intensity upon complexation with water. All values are computed at the MP2/aug-cc-pVDZ level. I_A , I_B , and I_C are the calculated rotational constants given in GHz.

Isomer	\mathfrak{R}_n	$\mathfrak{R}_{p\perp}$	$\mathfrak{R}_{p\parallel}$	I_A	I_B	I_C
H ₂ O...HCN	3.463 (2.51)	3.350 (2.52)	0.113 (2.35)	429.98	3.04	3.01
HCN...H ₂ O	2.606 (1.89)	2.464 (1.85)	0.142 (2.95)	476.62	3.25	3.23
CH ₃ HO...H ₂ O	4.424 (2.17)	4.403 (2.16)	0.021 (3.03)	24.92	4.62	4.05
CH ₃ OH...OH ₂	4.269 (2.09)	4.252 (2.09)	0.016 (2.39)	31.96	3.80	3.23

311 ++ G(d, p) [45]. For H₂O...HCN the binding energy has been obtained as 5.17 kcal mol⁻¹, whereas for HCN...H₂O the binding energy is found to be 3.38 kcal mol⁻¹, that is, 1.8 kcal mol⁻¹ smaller than for the first isomer. The existence of these isomers has also been detected by photolysis of formaldoxime [46]. In the case of the methanol–water isomers, both experimental techniques [47–49] and theoretical calculations [50] have predicted the existence of two stable heterodimers (figure 2). In this case, the CH₃HO...H₂O complex is found to be more stable than the CH₃OH...OH₂ isomer by an estimated amount less than 1 kcal mol⁻¹, or 0.7 kcal mol⁻¹ using the hybrid density-functional theory B3LYP/6-311 + G(3df, 2p) [50]. Here we find that CH₃HO...H₂O is more stable by 0.8 kcal mol⁻¹. In the theoretical study of these heterodimers by González *et al* [50], they obtained a hydrogen bond distance (O...H) in the case of CH₃HO...H₂O of 1.890 Å, and in the case of CH₃OH...OH₂ their value is 1.937 Å. These results compare favourably with our corresponding results of 1.904 and 1.942 Å, although our distances are slightly longer—by 0.014 and 0.005 Å, respectively. Our calculated Rayleigh scattering properties corresponding to these two groups of hydrogen bonded isomers are presented in tables 4 and 5.

As can be seen in table 4, although the polarizabilities and polarizability anisotropies of the hydrogen cyanide–water isomers are rather similar, the depolarization components of HCN...H₂O differ from those of H₂O...HCN by a factor of 1.7. However, this finding is not verified for the methanol–water isomers, for which the polarizabilities, anisotropies, and all components of the depolarization ratios have similar values. The variations in Rayleigh activities of the two groups of isomers are given in table 5. Again, the observed effect for \mathfrak{R}_n and $\mathfrak{R}_{p\perp}$ is strongly dominated by the $(\bar{\alpha})^2$ term, with a smaller contribution from the $(\Delta\alpha)^2$ term, whereas $\mathfrak{R}_{p\parallel}$ depends solely on the latter term. After complexation, these systems are of nearly-prolate rotor type, as indicated by the rotational constants (I_A , I_B , I_C) in table 5. These quantities are relevant for a millimetre wave description and have also been obtained previously, both theoretically [50] and experimentally [49]. In addition, the present accuracy might be useful in aiding possible detection of hydrogen bonded complexes [45].

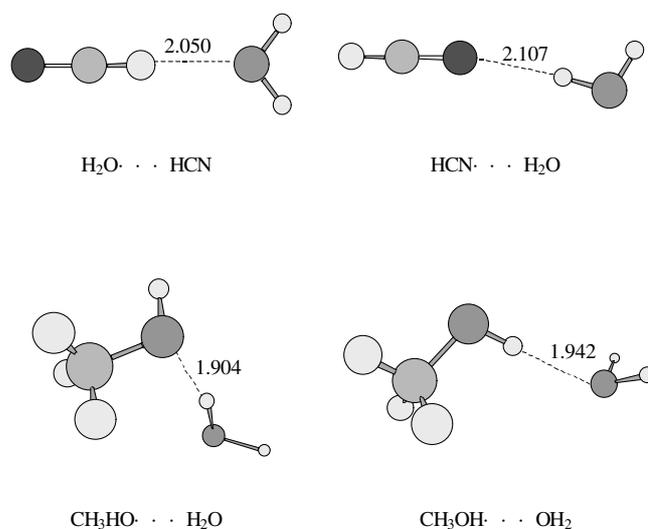


Figure 2. Structures of the HCN–water and methanol–water complexes. The lengths of the H bonds are given in Å, and were obtained at the MP2/aug-cc-pVDZ level.

4. Summary

A classical light scattering investigation has been made to analyse small hydrogen bonded clusters. Using *ab initio* calculations at the MP2/aug-cc-pVDZ level, full-geometry optimizations for different water complexes ($\text{H}_2\text{O} \cdots \text{H}_2\text{O}$, $\text{HCHO} \cdots \text{H}_2\text{O}$, $\text{CH}_3\text{HO} \cdots \text{H}_2\text{O}$, $\text{HCOOH} \cdots \text{H}_2\text{O}$, $\text{CH}_3\text{CN} \cdots \text{H}_2\text{O}$, and $(\text{CH}_3)_2\text{CO} \cdots \text{H}_2\text{O}$) have been performed. The dipole polarizabilities and polarizability anisotropies have been calculated for the separate molecules and the complexes. From these calculations, Rayleigh light scattering properties have been determined and compared, to analyse the changes upon hydrogen bond formation. The Rayleigh intensity is considerably increased by a factor of nearly two in most cases, with the exception of those of $(\text{CH}_3)_2\text{CO} \cdots \text{H}_2\text{O}$ and $(\text{H}_2\text{O})_2$. Different degrees of polarization have been considered (i.e., natural, plane-polarized, and circularly polarized light) to analyse the depolarization ratios. To assess depolarized Rayleigh scattering as a possible means of identifying intermolecular isomers, we have investigated the interaction between hydrogen cyanide (HCN) and water as well as methanol (CH_3OH) and water. Possible detections of these clusters have recently been of great interest in physical chemistry [46–49]. In the case of HCN the different isomers respond differently to light scattering, but in the case of methanol the distinction between the isomers is more difficult to discern in the scattering activity and in the depolarization.

References

- [1] Fabellinskii I L 1968 *Molecular Scattering of Light* (New York: Plenum)
- [2] Raman C V 1930 *The Molecular Scattering of Light (Nobel Lectures)* (Amsterdam: Elsevier) p 267
- [3] Buckingham A D 1967 *Adv. Chem. Phys.* **12** 107
- [4] Couling V W, Halliburton B W, Keir R I and Ritchie G L D 2001 *J. Phys. Chem. A* **105** 4365
- [5] Wilson E B Jr, Decius J C and Cross P C 1980 *Molecular Vibrations: the Theory of Infrared and Raman Vibrational Spectra* (New York: Dover)
- [6] Bush A M, Bell A J and Frey J G 1998 *J. Phys. Chem.* **102** 6457

- [7] Bell A J, Mestdagh J M, Berlande J, Biquard X, Cuvellier J, Lallement A, Meynadier P, Sublemontier O and Visticot J-P 1993 *J. Phys. D: Appl. Phys.* **26** 994
- [8] Teragishi Y and Aoki K 1999 *J. Electroanal. Chem.* **473** 132
- [9] Meulenbroeks R F G, Schram D C, Jaegers L J M and van de Sanden M C M 1992 *Phys. Rev. Lett.* **69** 1379
- [10] Park H S, Oh K S, Kim K S, Chang T and Spiegel D R 1999 *J. Phys. Chem. B* **103** 2355
- [11] Micali N, Trusso S and Vasi C 1996 *Phys. Rev. E* **54** 1720
- [12] Buckingham A D, Fowler P W and Hutson J M 1988 *Chem. Rev.* **88** 827
- [13] Curtiss L A and Pople J A 1975 *J. Mol. Spectrosc.* **55** 1
- [14] Diercksen G H F, Kraemer W P and Roos B O 1975 *Theor. Chim. Acta* **21** 249
- [15] Frisch M J, Pople J A and del Bene J E 1985 *J. Phys. Chem.* **89** 3664
- [16] Dykstra C E 1989 *J. Chem. Phys.* **91** 6472
- [17] Xantheas S S and Dunning T H Jr 1993 *J. Chem. Phys.* **98** 8774
- [18] Feyereisen M W, Feller D and Dixon D A 1996 *J. Phys. Chem.* **100** 2993
- [19] Engdahl A and Nelander B 1987 *J. Chem. Phys.* **86** 4831
- [20] Liu K, Cruzan J D and Saykally R 1996 *Science* **271** 929
- [21] Maroulis G 2001 *J. Phys. B: At. Mol. Opt. Phys.* **34** 3727
- [22] Bonin K D and Kresin V V 1997 *Electric-Dipole Polarisabilities of Atoms, Molecules and Clusters* (London: World Scientific)
- [23] Dixit S, Crain J, Poon W C K, Finney J L and Soper A K 2002 *Nature* **416** 829
- [24] Herzberg G 1945 *Infrared and Raman Spectra of Polyatomic Molecules* (Princeton, NJ: Van Nostrand-Reinhold)
- [25] Castro M A and Canuto S 1993 *J. Phys. B: At. Mol. Opt. Phys.* **26** 4301
- [26] Cernusak I, Diercksen G H F and Sadlej A J 1986 *Phys. Rev. A* **33** 814
- [27] Cohen H D and Roothaan C C J 1965 *J. Chem. Phys.* **43S** 34
- [28] Diercksen G H F and Sadlej A J 1988 *Chem. Phys. Lett.* **153** 93
- [29] Bartlett R J 1989 *J. Phys. Chem.* **93** 1697
- [30] Dunning T H Jr 1989 *J. Chem. Phys.* **90** 1007
- [31] Lovas F J 1978 *J. Chem. Ref. Data* **7** 1445
- [32] Frisch M J *et al* 1998 *GAUSSIAN 98 (Revision A7)* (Pittsburgh, PA: Gaussian Inc.)
- [33] Schütz M, Brdarski S, Widmark P O, Lindh R and Karlström G 1997 *J. Chem. Phys.* **107** 4597
- [34] Xantheas S S 1996 *J. Chem. Phys.* **104** 8821
- [35] Maroulis G 2000 *J. Chem. Phys.* **113** 1813
- [36] Tsuzuki S, Uchimaru T, Matsumura K, Mikami M and Tanabe K 1999 *J. Chem. Phys.* **110** 11906
- [37] Odutola J A and Dyke T R 1980 *J. Chem. Phys.* **72** 5062
- [38] Kirschner K N and Woods R J 2001 *J. Phys. Chem. A* **105** 4150
- [39] Wei D, Truchon J-F, Sirois S and Salahub D 2002 *J. Chem. Phys.* **116** 6028
- [40] Rivelino R, Ludwig V, Rissi E and Canuto S 2002 *J. Mol. Struct.* **615** 259
- [41] Coutinho K, Saavedra N and Canuto S 1999 *J. Mol. Struct.* **466** 69
- [42] Lide R (ed) 1992 *Handbook of Chemistry and Physics* 73rd edn (Boca Raton, FL: Chemical Rubber Company Press)
- [43] Zhou T and Dykstra C E 2001 *J. Physique A* **104** 2204
- [44] Nakagawa S 1997 *Chem. Phys. Lett.* **278** 272
- [45] Rivelino R and Canuto S 2000 *Chem. Phys. Lett.* **322** 207
- [46] Heikkilä A, Pettersson M, Lundell J, Khriachtchev L and Räsänen M 1999 *J. Phys. Chem. A* **103** 2945
- [47] Huisken F and Stemmler M 1991 *Chem. Phys. Lett.* **180** 355
- [48] Bakkas N, Bouteiller Y, Louteiller A, Perchard J P and Racine S 1993 *J. Chem. Phys.* **99** 3335
Bakkas N, Bouteiller Y, Louteiller A, Perchard J P and Racine S 1995 *Chem. Phys. Lett.* **232** 90
- [49] Stockman P A, Blake G A, Lovas F J and Suenran R D 1997 *J. Chem. Phys.* **107** 3782
- [50] González L, Mó O and Yáñez M 1998 *J. Chem. Phys.* **109** 139