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Michel Mons; Iliana Dimicoli; François Piuzzi

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## Gas phase hydrogen-bonded complexes of aromatic molecules: photoionization and energetics

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The present review discusses the possibility of measuring the dissociation energy of gas phase complexes from their dissociative photoionization. A compilation of recent results on hydrogen-bonded complexes of aromatic molecules, with a polar solvent molecule (water, alcohol, NH<sub>3</sub>, HCl, etc.), playing the role of either proton donor or proton acceptor is presented. We show that laser experiments begin to provide a consistent set of energetic data that can be considered as benchmarks to assess quantum calculations as well as to parametrize the force field models used in biochemistry.

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## 1. Introduction

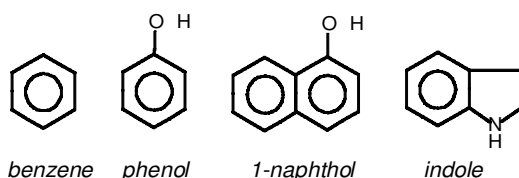
The precise knowledge of the energetics of intermolecular bonds has become a crucial issue with the development of molecular mechanics simulation and the increased demand for H-bond benchmark data for model potential parametrization, especially in biochemistry. However, until the last few years, only a few experimental data were available and parametrization has stemmed mainly from *ab initio* calculations, whose reliability strongly depends on the nature of the interactions at play in the system and on the method used, generally adapted to the calculation facilities (execution times, memory, mass memory, etc.) (Dunning 2000, Rappé and Bernstein 2000). In practice, these calculations require benchmark systems to validate the level of theory or the size of the basis sets used as well as to estimate their precision. This can indeed be crucial in systems where dispersive interactions cannot be neglected, and which therefore require electronic correlation to be taken into account explicitly, as well as the use of very extended basis sets. Similarly, the prediction of the relative energy of two conformers of a molecular complex, having different types of bonding, for example,  $\sigma$ - and  $\pi$ -type hydrogen bonds is also a difficult issue. The latter bond being dominantly driven by dispersive forces, its calculation requires more attention and its strength is usually difficult to scale relative to bonds controlled by electrostatics.

Experimental determination of the interaction energy between molecules and more generally the question of the shape of the intermolecular potential surface is a long-standing topic. Beginning with the van der Waals' studies of gases and their departure from the ideal gas behaviour (Curtiss and Blander 1988), a wealth of techniques have been developed in order to collect information on intermolecular potentials. Unfortunately, the major part of them (studies of virial coefficients, transport properties, vibrational spectroscopy of molecular complexes, molecular beam scattering, etc.) provide only indirect information on the potential shape, requiring further work to extract the relevant information (Buckingham *et al.* 1988, Stone 1996).

With the development of the supersonic expansion technique, that has allowed experimentalists to form and study weakly bonded intermolecular complexes (Levy *et al.* 1982, Legon and Millen 1986), a wealth of spectroscopic data are available nowadays (Felker 1992, Zwier 1996, Brutschy 2000, Dessent and Müller-Dethlefs 2000). For example, the structure of these complexes is often determined to a good accuracy by rotational spectroscopy from the rotational constants (Leopold *et al.* 1994, Pratt 1998). Energy, however, is also a relevant parameter for knowledge of the potential energy surface close to its minima and for the comparison with theoretical results. The centrifugal distortion constant, also derived from rotational spectroscopy, can be used for estimating the interaction energy, but the method greatly depends on the shape assumed for the potential energy surface, which is unfortunately not well known.

For these reasons, techniques applied to gas phase complexes, providing precise and direct energetic information on the potential surface itself, are of great interest, even if the value measured, the dissociation energy  $D_0$ , is not directly comparable with the interaction energy  $D_e$ , that theoreticians derive first. Such measurements remain sparse (Neusser and Krause 1994, Haas and Kendler 1997), probably because of the difficulty of the experiments involved.

In the present review, we shall focus on those spectroscopic laser techniques that provide one of the major energetic data, i.e. the 0K dissociation energy  $D_0$  of hydrogen-bonded complexes, in particular 1:1 hydrates of aromatic molecules, whose resemblance to hydration sites of aromatic residues in proteins (Duan *et al.* 2000, Steiner and Köllner 2001) makes them relevant to biochemistry modelling (Desfrancois *et al.* 2000, Robertson and Simons 2001).



An important section will be devoted to photoionization and its variants (one- or two-photon, one- or two-colour), with a marked attention on the distribution of vibrational energy deposited in the ion and the possibility of measuring energetic values from photoionization-induced dissociation. Recent experimental results on hydrogen-bonded complexes of aromatic molecules will be discussed and compared with the most recent theoretical calculations, with special attention paid to benchmark systems such as complexes of benzene (Bz).

## 2. Experimental energetic measurements on jet-formed complexes

### 2.1. Photoionization of H-bonded complexes

#### 2.1.1. Seeking for selectivity

The first experiments of (one-photon and hence one-colour) photoionization (ICPI) of hydrogen-bonded complexes combining supersonic jet and synchrotron radiation were carried out at Brookhaven and Berkeley. Jet-cooled molecules as well as homodimers and/or heterodimers have been photoionized and detected by time-of-flight mass spectrometry (Ng *et al.* 1977, Ng 1991, Grover *et al.* 1985, 1987, 1988, 1989, 1990, 1992) and reactivity studies on the ion have been performed (Ng *et al.* 1977, Grover *et al.* 1990, Dedonder-Lardeux *et al.* 1995). However, the one-photon process used is not very selective (Berkowitz 1979) since the photon energy is the only selecting factor: contributions of all the species present in the jet are therefore expected if the photon energy is larger than their ionization energy.

With the development of pulsed ultraviolet (UV) lasers, resonant two-photon ionization (R2PI) of atoms and molecules has been made possible. Furthermore, the first step of R2PI, which consists in an electronic excitation of a well-defined species, can be very selective. Since the electronic transitions of molecules and complexes are usually size, and even conformer dependent, with bands spectrally separated by 1–1000  $\text{cm}^{-1}$  depending on the interactions at play (Bernstein 1990, Topp 1993,

Brutschy 2000, Robertson and Simons 2001, Zehnacker *et al.* 1994), the use of a pulsed commercial frequency-doubled dye laser (*ca.*  $0.3 \text{ cm}^{-1}$  spectral width) enabled experimentalists to achieve a significant selectivity among the several species coexisting in a jet. The second step, which is the ionization step itself, is similar to the one-photon photoionization process and occurs during the same laser pulse (one-colour R2PI ; figure 1(a)) or can be performed using a second laser pulse within the lifetime of the excited state populated by the first pulse (two-colour R2PI, figure 1(c)).

The R2PI process opened up a series of possible photoionization experiments on size- and conformer-selected complexes that address several physical and chemical problems, such as the effect of solvation on the molecular properties (Bernstein 1990, Zwier 1996) or on its chemical reactivity (Brutschy 1992, Dedonder-Lardeux *et al.* 2000). Aromatic molecules, which often have an excited electronic state located midway from their ionization potential, have been extensively studied by this technique, and, because of this very convenient property, most of the laser work on dissociation energies carried out so far has been done on complexes of aromatic molecules.

### 2.1.2. Pushing further the selectivity

In addition to the isomer and size selectivity brought by the R2PI process, experimentalists have tried to characterize and select the photoions formed, in particular to obtain information on their vibrational energy distribution. Several techniques have been developed, all of them based on the two principles controlling the ion formation: (i) the energy conservation of the system (molecule + photon) and (ii) the Franck–Condon (FC) principle, since, as any optical transition, photoionization ( $S_0 \rightarrow \text{ion}$  transition for 1CPI;  $S_1 \rightarrow \text{ion}$  for R2PI) obeys this basic principle. The distribution of vibrational levels accessible in the ion by R2PI is determined by the FC factors: depending on the change in equilibrium geometry between the neutral  $S_1$  state and the ion, narrow or wide distributions of vibrational levels can be formed, with a corresponding mirror distribution of photoelectron energies, since the energy

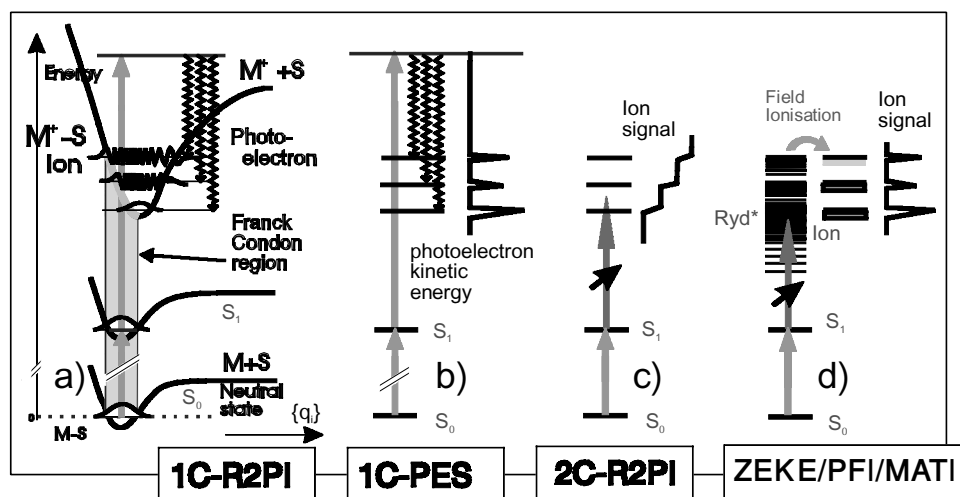


Figure 1. (a) Scheme of the potential energy curves of complexes relevant to one-colour photoionization (1C-R2PI); shape of the signal expected for (b) one-colour R2PI photoelectron spectroscopy, (c) two-colour R2PI and (d) zero kinetic energy (ZEKE) based techniques.

difference between the final ion state and the two-photon energy is carried away by the photoelectrons (figure 1(a)).

A first way to select the ions consists in scanning the photon energy (figure 1(c)). This technique coupled to mass spectrometry leads to the measurement of ionization thresholds in 2C-R2PI experiments (Duncan *et al.* 1981, Fung *et al.* 1981). This technique turns out to be much more interesting than one-photon photoionization for studying jet-formed complexes since the resonant step ensures some species selectivity. The spectra obtained are a cumulative sum over the distribution of the FC-accessible vibrational levels of the ion.

A second way consists of selecting the photoelectrons. This can be achieved by several techniques. One can measure the photoelectron distribution for a fixed photon energy in a 1C-R2PI experiment (laser photoelectron spectroscopy (laser PES)), which is a laser variant of classic PES (Turner *et al.* 1970, Long *et al.* 1983, Fuke *et al.* 1984, Weinkauff *et al.* 2000) (figure 1(b)): for a fixed photon energy, one determines the distribution of photoelectrons and therefore the distribution of ion internal vibrational energy. Alternatively, in a 2C-R2PI experiment, one can scan the photon energy, whereas only threshold photoelectrons are collected, which is, in some respects, similar to the classic threshold PES of the synchrotron radiation community (Baer and Guyon 1995). Recent developments consisting of collecting only electrons, using a more or less sophisticated delayed pulsed-field ionization technique of highly excited Rydberg states, has given birth to ZEKE spectroscopy (Müller-Dethlefs *et al.* 1984) that also provides the internal energy distribution in the photoion (figure 1(d)). This active field has recently been reviewed (Müller-Dethlefs and Schlag 1991, Held and Schlag 1998, Dessent and Müller-Dethlefs 2000). A derived procedure, which detects the photoions after distinguishing pulsed-field ionized Rydberg excited molecules from the ionization background in a time-of-flight mass spectrometer, has also been developed (Krause and Neusser 1993, Dessent *et al.* 1999). In this case, one performs a mass-analysed threshold ionization (MATI). These three techniques, all of them based on ionization at threshold, provide reliable insight into the distribution of the FC-accessible levels of the ion.

### 2.1.3. Photoionization of molecules and complexes close to the threshold

For a long time, the vibrational activity as determined by the shape of the photoionization curve at threshold or by the shape of the internal energy distribution (as obtained from PES for example) has been recognized as a signature of the change in equilibrium geometry between neutral and ion (Herzberg 1950). Adiabatic thresholds, characterized by steep thresholds in the photoionization curves or by strong and by intense and well-resolved origin bands in PES, are assigned to negligible geometry changes and narrow FC 'window' (Turner *et al.* 1970, Berkowitz 1979). To take an example among aromatic molecules, phenol or indole exhibits such a typical adiabatic behaviour with negligible vibrational activity: the band origin of the ionization transition is by far the most prominent and the aromatic cation is formed with negligible vibrational energy (Turner *et al.* 1970, Müller-Dethlefs *et al.* 1994).

In contrast, ill-defined photoionization thresholds or bell-shaped FC distributions evidenced by PES, featuring a non-adiabatic behaviour, are a signature for qualitative differences in structure between neutral and ionic states. Folded conformations of flexible molecules such as 1- or 2-phenylethanol do belong to this class,

with their ground vibrationless level of the ion not accessible by photoionization (Weinkauff *et al.* 2000, Mons *et al.* 2000a).

In this respect, Bz exhibits an intermediate behaviour: because of the Jahn–Teller distortion of its two-fold degenerate ionic electronic ground state, a broad FC distribution is observed in the cation (Long *et al.* 1983), but nevertheless the cation origin is fairly accessible to photoionization (Duncan *et al.* 1981, Fung *et al.* 1981).

For the complexes, photoionization curves were measured using 2C-R2PI as early as in the 1980s. Whereas complexes with polarizable species, such as rare gases, exhibit steep adiabatic thresholds that mimic those of the corresponding aromatic molecule, for instance Bz–argon (Fung *et al.* 1981) and indole–argon (Hager *et al.* 1986), hydrogen-bonded complexes have been shown to behave differently in terms of vibrational energy deposited in the ion.

Much work has been carried out on the photoionization of the archetypal hydrogen-bonded phenol–water complex (figure 2(a)), starting with the early work of Lipert and Colson (1988). The successive steps in the R2PI photoionization curve, as well as the nice progression in the ZEKE spectrum (Dopfer *et al.* 1994, Müller-Dethlefs *et al.* 1994), have been assigned to successive excitations of the H bond stretch mode of a complex cation, similar in geometry to the neutral complex. One can notice, for R2PI, that the FC principle applies to the ionization step and therefore one should compare the ion with the  $S_1$  neutral complex. However, owing to the usual similarities of the  $S_0$  and  $S_1$  complexes of aromatic molecules, as well as the difficulty in calculating reliable excited state structures, the neutral ground state is often used as the neutral reference. *Ab initio* calculations have confirmed this picture, yielding to a shrinkage of the OH—O bond by 0.04 Å on ionization (Dopfer

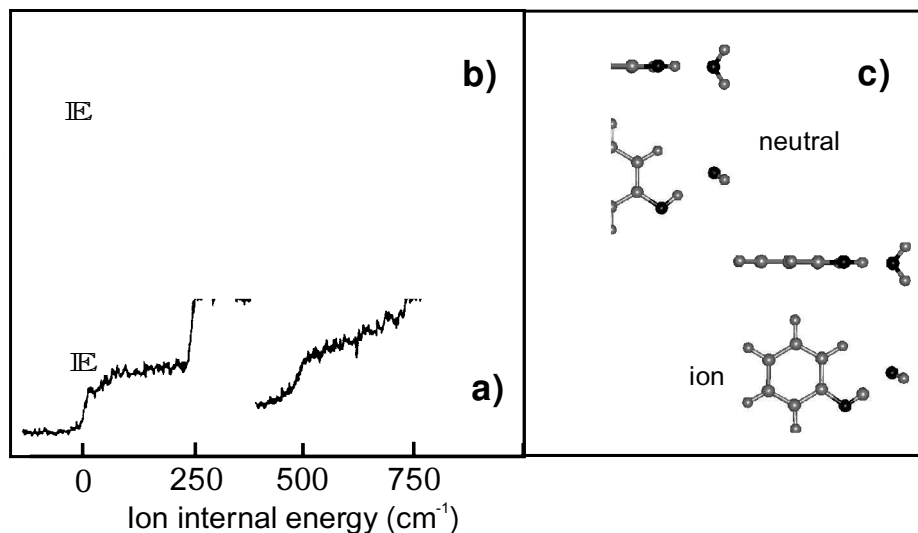


Figure 2. Phenol–H<sub>2</sub>O complex: (a) photoionization curve as obtained by two-colour R2PI (reprinted with permission from Lipert and Colson, *Journal of Chemical Physics*, **89**(8), 1988, pp. 4579–85, © 1988, American Institute of Physics) and (b) corresponding ZEKE spectrum (reprinted with permission from Dopfer *et al.*, *Journal of Chemical Physics*, **101**(2), 1994, pp. 974–89, © 1994, American Institute of Physics); (c) minimum energy conformations of the neutral and ionic complex, as obtained by a semi-empirical model (Courty *et al.* 1998a).

*et al.* 1994). Because of favourable FC factors, the origin band is one of the most intense features (figure 2(b)), and the FC envelope of accessible levels does not extend beyond  $1500\text{ cm}^{-1}$ .

In contrast, several other H-bonded species have been shown to exhibit photoionization curves of a very different type, characterized by slowly rising ill-defined onsets. Ito and coworkers have shown first such behaviour for the complexes of fluorobenzene with water,  $\text{CH}_3\text{Cl}$ , etc. (Gonohe *et al.* 1985). Other complexes were found to belong to the same class, in particular the Bz dimer (Grover *et al.* 1987, 1989, Selzle *et al.* 1989) and the H-bonded complexes of Bz with HCl (Walters *et al.* 1985) and water (Cheng *et al.* 1995, Courty *et al.* 1998b). The slowly rising onset of the Bz–water complex is depicted in figure 3(a). In all cases large qualitative equilibrium geometry changes and therefore unfavourable FC factors were evoked to interpret these ill-defined photoionization thresholds. This explanation is supported by calculations (Kim *et al.* 2000, Courty *et al.* 1998b). The neutral Bz–water complex is predicted to be a  $\pi$ -type H-bonded system, in which Bz acts as a proton acceptor with two water hydrogens pointing toward the ring (figure 3(b)). In contrast, the ionic species exhibit a very different ionic potential energy surface: two minima are found, one with the water in the equatorial plane of Bz, and a second minimum with the water molecule above the ring but flipped over relative to the neutral (figure 3(b)).

In a more generalized picture, as far as the vibrational energy deposited in the ion is concerned, two basic types of hydrogen bonded aromatic molecule–polar solvent (M–S) complexes can be described, depending on the nature of M, namely its proton acceptor or donor character in the complex.

Photoionization of an H-bonded complex of an aromatic molecule leads to the ejection of a  $\pi$  electron of the aromatic ring. In the complex ion, this charge is

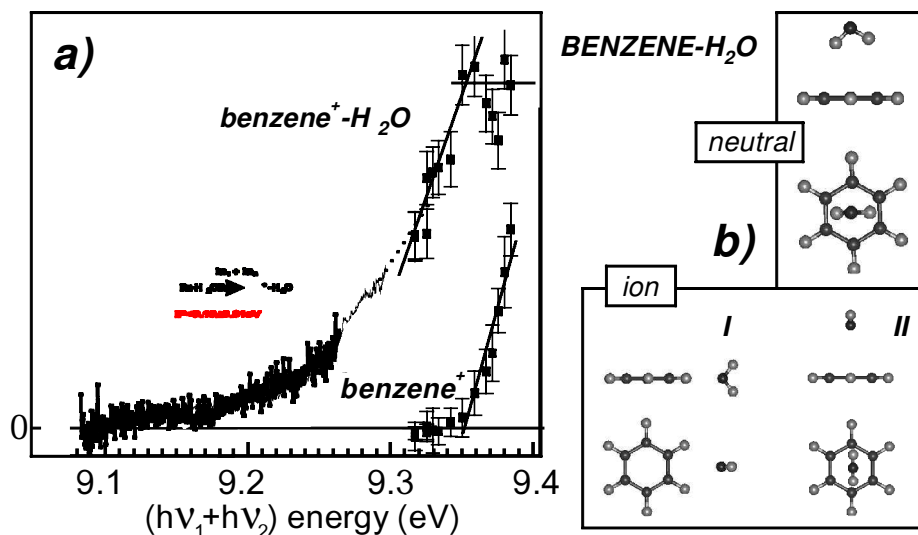


Figure 3. Benzene– $\text{H}_2\text{O}$  complex: (a) photoionization curve as obtained by two-colour R2PI, showing the onsets of both photoionization and fragmentation; (b) minimum energy conformations of the neutral and ionic surfaces, as obtained by a semi-empirical model (adapted from Courty *et al.* 1998b).



responsible for a qualitative change in the electrostatic interaction, with the triggering of a new intense charge–dipole interaction. Depending on the orientation of the solvent molecule in the neutral, two limiting cases can be expected for photoionization.

With a proton-donating aromatic molecule (case of phenol; figure 2(c)), the solvent dipole is mainly pointing outside the aromatic molecule, according to the polarization of the H bond. On ionization the H bond is stabilized by the charge–dipole interaction: the ion conformation is very similar to that of the neutral (Courty *et al.* 1998a). Ions formed by photoionization (figure 4(a)), according to the FC principle applied to the intermolecular modes, present a narrow vibrational distribution of intermolecular modes, with the vibrationless level being significantly populated. This must be linked to the adiabatic features of the photoionization curve of this type of complex (figure 2(a)).

With a proton acceptor molecule such as Bz, the dipole of the solvent molecule usually points towards the ring, a structure which is very destabilized in the ion because of the charge–dipole interaction (figure 3(b)) (Courty *et al.* 1998b). The ion structure is therefore very different from the neutral one, with a flipped over water molecule. The ions formed all exhibit a strong excitation of their intermolecular vibrational levels and the vibrational ground level is not accessible (non-adiabatic ionization, figure 4(b)). For a complex such as Bz–water (figure 3(b)), it has been shown that the neutral equilibrium conformation (vertical ionization) leads to a local maximum of the potential energy surface, situated above the dissociation limit of the complex ion (Courty *et al.* 1998b). The same study has shown that the neutral conformations responsible for the threshold ionization are associated to the wings of the ground state vibrational wave function corresponding to water molecules

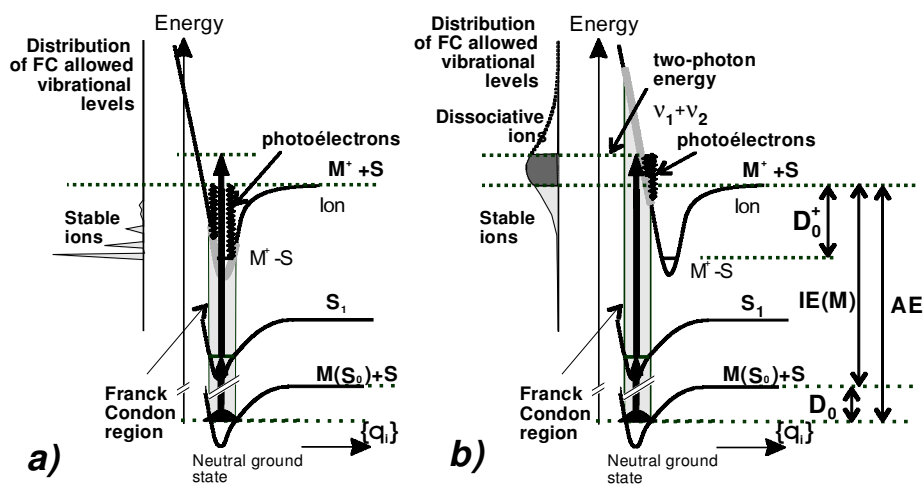


Figure 4. Energetic scheme of two-colour resonant two-photon ionization, showing photoelectrons the FC region and the distribution of FC-allowed vibrational levels in the ion. (a) Adiabatic ionization (limiting case phenol–water): the ionic equilibrium geometry is accessible and no fragmentation is expected. (b) Non-adiabatic photoionization (limiting case benzene–water): the ionic vibrationless level is not accessible; only vibrationally excited levels are formed and significant fragmentation is expected.

displaced from the Bz C<sub>6</sub> axis and having their permanent dipole nearly parallel to the Bz ring. Such a picture is supported by the quantum Monte Carlo vibrational wave functions obtained by Gregory and Clary (1996) for this system.

The above presentation is thought to be a general picture. However, phenol–water and Bz–water are likely to be limiting cases and most other complexes will exhibit behaviour somewhere between these two extremes. As an example, compared with phenol–water, phenol–methanol and phenol–ethanol species are known to show much more dense and barely resolved structures (Dopfer *et al.* 1994). *Ab initio* calculations without electronic correlation could not account for the effect. Recent semi-empirical calculations (Courty *et al.* 1998a), taking dispersion into account, could shed some light on this issue. In the neutral, alkyl ring dispersive forces are large enough to bend the H bond slightly, whereas this does not occur in the ion because of the strong charge-enhanced electrostatic interaction. As a consequence neutral–ion FC factors are no longer favourable for adiabatic ionization. This picture was recently supported by rotationally resolved data on the phenol–methanol system (Schmitt *et al.* 2000, Kupper *et al.* 2001) that provided spectroscopic evidence for a tilted and displaced methanol molecule compared with the symmetric arrangement of water in phenol–water.

The above discussion is centred on the *intermolecular* modes, which are mostly responsible for the ion distribution. For the sake of thoroughness, one should also mention the role of the *intramolecular* modes of the aromatic molecule that can be excited in combination with intermolecular modes.

#### 2.1.4. One-colour R2PI photoionization and dissociation

The vibrational energy deposited in the complex ion following an R2PI process is *a priori* available for vibrational predissociation (fragmentation or evaporation, in the terminology of mass spectroscopists), as soon as this energy overcomes the complex ion dissociation limit.

More than a decade ago, Zwier's group observed that the Bz hydrates give rise to intense fragmentation following 1C-R2PI (Gord *et al.* 1990). Fragmentation ratios ( $[\text{fragment ions}]/[\text{parent} + \text{fragment ions}]$ ) as large as 85% were measured on these systems (Courty *et al.* 1998b). Such a large efficiency is generally considered as an unpleasant process that affects the mass-selective character of R2PI combined with mass spectrometry, generally sought by cluster spectroscopists keen to obtain mass-selective cluster data. This phenomenon has led for instance to several misassignments, especially for the aromatic–water clusters (Bz–NH<sub>3</sub>, Bz–H<sub>2</sub>O (Bernstein 1990)). One can mention at this point that spectroscopists became aware of these problems and that subtle techniques involving appearance times in the pulsed supersonic expansion were extremely useful for assigning bands in terms of cluster size (Li and Bernstein 1992, Yao *et al.* 2000 and references therein).

However, not all the H-bonded species tend to fragment on ionization. Fragmentation of phenol complexes, for instance, was usually neglected, since it was never considered as a cause of spectral pollution.

From a general point of view, fragmentation essentially comes from the efficiency of the photoionization process in producing vibrationally excited complex ions, beyond the dissociation limit. As seen before, this is mainly controlled, for R2PI, by FC factors between the S<sub>1</sub> state and ion for both the intermolecular and the intramolecular modes. After formation of these highly excited levels, intracuster vibrational redistribution (IVR) takes place and leads to dissociation.

For complexes of proton donor molecules, such as phenol, the FC distribution of intermolecular vibrational levels remains close to the ionic well bottom (figure 4(a), case of an adiabatic ionization). ZEKE spectroscopy shows that this distribution does not extend significantly beyond  $2000\text{ cm}^{-1}$  (Müller-Dethlefs *et al.* 1994). From such a basic idea, one would expect the phenol–water complex not to dissociate. Furthermore, 1C-R2PI measurements via the  $S_1 \rightarrow S_0$  origin transition led to a fragmentation ratio of 10% for the phenol–water complex (Courty *et al.* 1998a). This value cannot be understood on the basis of the FC principle on the intermolecular modes alone. Owing to the dissociation energy of the ion ( $\sim 7000\text{ cm}^{-1}$  (Courty *et al.* 1998a)), dissociation is caused by excitation of both intermolecular and intramolecular modes of the cation. In the latter case IVR occurs, converting the intramolecular vibration into additional intermolecular vibrational excitation.

For complexes of proton acceptor molecules, such as Bz–water, photoionization leads mainly to ion conformations lying above the dissociation limit (figure 4(b), case of a non-adiabatic ionization). Only those conformations that belong to the lower part of the FC distribution may produce vibrationally excited but stable (i.e. non-dissociative) photoions. One can notice that, in this case, the intramolecular cation excitations still increase the fragmentation process owing to the molecular geometry change.

As a general result, it turns out that the fragmentation properties are intimately linked to the direction of the H bond in the complex. Although it has an apparent qualitative nature, the simple principle that has led us to this conclusion is supposed to hold for any photoionized molecule (not only aromatic), and any type of H bond. This is obviously supported by the fragmentation ratio known for the complexes of phenol and Bz; the apparent exception of indole (Mons *et al.* 1999) is due to the existence of a low-lying electronic state in indole<sup>+</sup>, which is widely populated by photoionization and therefore increases the fragmentation process.

We believe that the fragmentation properties on photoionization, in particular the fragmentation ratio in the 1C-R2PI experiment, can bring qualitative but valuable clues to the structure of the complexes studied, in particular about the direction of the H bond. This expectation was very recently demonstrated in the case of *N*-phenyl formamide (formanilide), an aromatic molecule exhibiting an amide group, for which two hydration sites can be expected, the amide group being either donor or acceptor (figure 5). These sites have been detected as individual complexes in a supersonic jet by UV spectroscopy (Dickinson *et al.* 1999, Fedorov and Cable

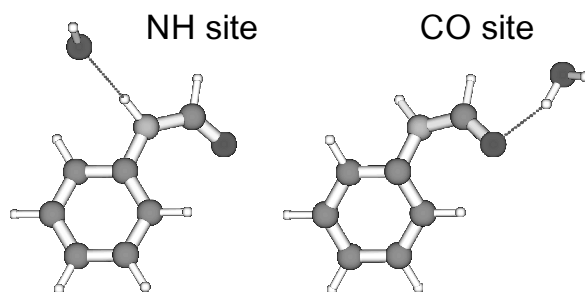


Figure 5. *Ab initio* geometries of the two 1:1 hydrates of the *trans* isomer of formanilide, predicted by MP2/6-311+G\*\* calculations. The NH site complex is found to fragment less (22%) than the CO site complex (47%) (Mons *et al.* 2000b).

2000). The assignments as obtained from their fragmentation ratios (22% and 47%) in a 1C-R2PI experiment (Mons *et al.* 2001) satisfactorily matched those obtained from infrared (IR) spectroscopy (Robertson 2000).

### 2.1.5. Energetic measurements from dissociative photoionization

Fragmentation of vibrationally excited ionic complexes formed by photoionization can also be used for energetic measurement purposes. Since the photon energy selects the distribution of ions formed, scanning the photon energy allows the experimentalist to detect the threshold for ionic fragmentation. A simple energetic balance leads to the energetics of the neutrals.

*Two-colour dissociative photoionization (DPI) measurement.* In a 2C-R2PI scheme, the complexes (M-S) are photoexcited selectively by a first laser. The second colour is then scanned in the dissociation region of the complex (M<sup>+</sup>-S) until fragmentation into M<sup>+</sup> + S can be monitored in the mass spectrometer. The dissociation energy  $D_0$  of the neutral ground state complex is deduced from the difference between the appearance energy AE of the M<sup>+</sup> ion and the adiabatic ionization energy IE<sub>ad</sub> of the molecule M (figure 4):

$$D_0 = \text{AE}(\text{M}^+\text{-S} \rightarrow \text{M}^+ + \text{S}) - \text{IE}_{\text{ad}}(\text{M} \rightarrow \text{M}^+). \quad (1)$$

The use of the 2C-R2PI scheme also allows the S<sub>1</sub> state dissociation energy to be derived as a side product of the measurement from the spectral shift  $\delta\nu$  of the S<sub>1</sub> – S<sub>0</sub> transition in the complex:

$$D_0(\text{S}_1) = D_0 - \delta\nu. \quad (2)$$

When the adiabatic ionization energy IE<sub>ad</sub> of the complex can also be determined, the dissociation energy of the ionic complex  $D_0^+$  can also be deduced from

$$D_0^+ = \text{AE}(\text{M}^+\text{-S} \rightarrow \text{M}^+ + \text{S}) - \text{IE}_{\text{ad}}(\text{M-S} \rightarrow \text{M}^+\text{-S}). \quad (3)$$

One will notice that procedures (1) and (3) require respectively that the measurement of the *adiabatic* ionization energy of the molecule and that of the complex are feasible.

When the adiabatic ionization threshold of the molecule M is not observed, the adiabatic threshold of the complex also cannot be observed since intramolecular FC factors of the complex are similar to those of the molecule. In this case, one determines only a lower limit for both the neutral and the ion dissociation energies ( $D_0$  and  $D_0^+$ ) (Mons *et al.* 2000a). This point is not always taken into account and leads to several more or less severe underestimations (Longarte *et al.* 2000, Satta *et al.* 2000, Unamuno *et al.* 2000, Fernández *et al.* 2001). However, comparison of two complexes of the same molecule M remains valid. Indeed, the absolute error on  $D_0$  arises from the incorrect IE<sub>ad</sub> chromophore molecule alone, and therefore relative dissociation energies of complexes are still meaningful (Mons *et al.* 2000a).

When the adiabatic ionization threshold of the molecule M is known but when M is a proton acceptor, the adiabatic photoionization threshold of the complex is generally not measurable. Then only ion dissociation energy ( $D_0^+$ ) measurements are affected. Again, neglecting this point, for instance in the case of Bz-water, generated severe underestimates of the ionic binding energy (Cheng *et al.* 1995).

This type of experiment can be conducted for those systems in which the FC distribution of ionic vibrational levels encompasses the fragmentation limit. If this is kept in mind, 1C-R2PI experiments discussed above are useful to test the feasibility

of the measurement. Owing to the energy of the  $S_1$  state of these species, the two-photon energy of the 1C-R2PI process usually overcomes the upper limit of the FC region in the ion, so that one-colour experiments produce all the vibrational levels accessible in the ion. Finally, one can notice that the ionic system must also not be reactive; in such a case, indeed, the reactive channels would possibly compete with fragmentation in the ionic excited vibrational level and may suppress it.

*Two-colour DPI: practical considerations.* In practice, 2C-DPI monitors the fragmentation in a mass spectrometer, usually of the time-of-flight type. Figure 6 shows that the experiment can be carried out either by collecting all the fragment ions formed or by selecting them, for instance, in a MATI experiment, since fragmentation has been shown not to induce the detachment of the Rydberg electron (Krause and Neusser 1993). The two types of signals expected are shown in figure 6 (a) and (b) in the case of a non-adiabatic photoionization process.

The R2PI signal, which is the *cumulative sum* over the FC-accessible vibrational levels of ions having an energy lower than the photon energy, increases monotonically with the photon energy until the dissociation limit is reached. A plateau is then reached and the amount of stable complex ion no longer increases. The complex ions formed beyond this limit are all dissociative: they are detected in the fragment  $M^+$  mass channel and their intensity follows the photoionization curve of the parent ions. The fragmentation threshold is therefore determined as the onset of the fragment signal. As an example, figure 3(a) shows the signal of  $Bz^+-H_2O$  and  $Bz^+$  ions formed on 2C-R2PI, with the plateau of the parent signal that corresponds to the onset of the fragment. A typical precision of  $\sim 0.15$  kcal mol $^{-1}$  (about 50 cm $^{-1}$ ) is currently achieved, especially when the fragmentation ratio instead of the absolute fragment signal is plotted, since it enables one to avoid the effects of laser fluctuations.

The MATI signal is sensitive to the *density* of FC-accessible states so that at the fragmentation threshold the parent signal vanishes to the benefit of the fragment signal. As an example, the MATI spectrum of phenol-CO (figure 7) shows that the density of states accessible in the fragmentation region is not always very high, but

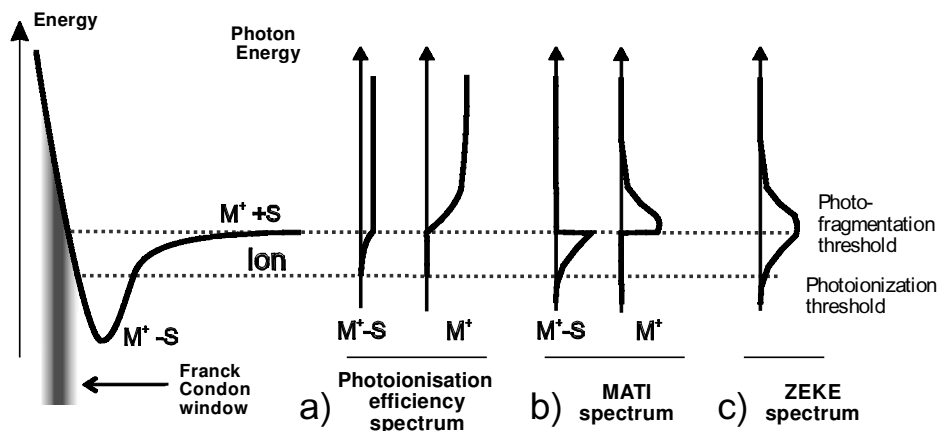


Figure 6. Shape of signal variations expected as the energy of the ionization photon ( $h\nu_2$ ) is increased in a dissociative two-colour R2PI experiment (non-adiabatic case) for three detection schemes: (a) photoionization with mass selection, (b) mass-analysed threshold ionization and (c) ZEKE electron spectroscopy.

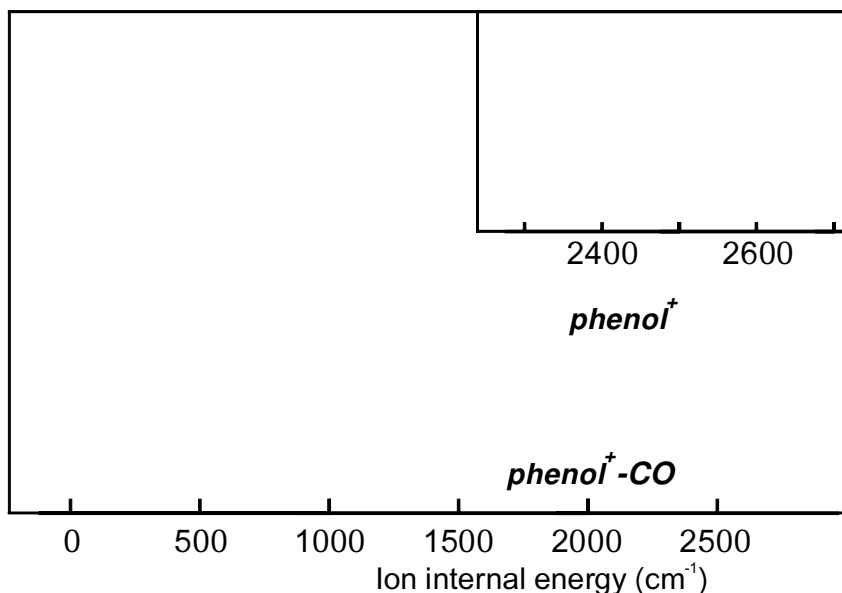


Figure 7. MATI dissociation spectrum of  $\text{phenol}^+-\text{CO}$  recorded via the  $S_10^0$  band origin. The insert shows an expanded plot of the dissociation region with the broken line indicating the position of the field-free ionic dissociation threshold (reprinted with permission from Haines *et al.*, *Journal of Chemical Physics*, **111**(5), 1999, pp. 1947–54, © 1999, American Institute of Physics).

the simultaneous detection of the parent vanishing and daughter onset makes it a very precise technique, even if the magnitude of the electric field is expected to lower its resolution (Grebner *et al.* 1997, Dessent and Müller-Dethlefs 2000). Resolutions of *ca.*  $20\text{ cm}^{-1}$  are currently reported.

This points out the fact that the MATI measurement is *stricto sensu* a bracketing of the dissociation limit and that the 2C-R2PI experiment yields an upper bound of the dissociation limit. This can become a major drawback of these techniques when the density of FC-allowed levels is low, as in pure van der Waals systems because of the weak FC activity of the intermolecular modes. In contrast to the rather favourable case of  $\text{phenol}-\text{CO}$  (figure 7), only an upper limit of the dissociation energy of  $\text{Bz}-\text{Ar}$  was deduced from a reasoning including both neutral and ionic data on the  $\text{Bz}-\text{Ar}$  and  $\text{Bz}-\text{Kr}$  species (Krause and Neusser 1993). Such a problem generally does not occur with  $\pi$ -bonded systems since in this case one reaches very high regions of the ion PES, at energies where the density of FC-accessible states is large. Conversely, in very unfavourable systems (non-adiabatic ionization), one could possibly observe no stable ions because all the ions formed are dissociative. In such a case, relation (1) would only provide an upper limit of the neutral dissociation energy.

The detection of the fragment ions assumes that the lifetime of the dissociative ions is short, i.e. shorter than the time window of the mass spectrometer used, which is usually in the microsecond time range for time-of-flight mass spectrometry. Owing to the small size of the complex, dissociation is expected to occur in less than 100 ns as soon as the excess energy above the dissociation limit is larger than a few tens of  $\text{cm}^{-1}$ . This possible source of error, the ‘kinetic shift’ in mass spectrometry (Baer

and Hase 1996), is thought to be negligible for small-size complexes. In particular, Bz<sub>2</sub> dissociation energies obtained by collecting the ions without (Courty *et al.* 1998b) or with the 'metastable' long-lived ionic species (with a reflectron-type mass spectrometer (Ernstberger *et al.* 1990)) are not significantly different. However, kinetic shifts probably do need to be taken into account for cluster sizes larger than four molecules (Klots 1985, Spangenberg *et al.* 2000). At this stage, it is worthwhile to notice that no barrier to dissociation is assumed in the measurement procedure. This point, doubtless in small complexes, such as 1:1 hydrates, is, however, less straightforward when the system size increases. One also assumes that, in case of a combined primary excitation of *intermolecular* and *intramolecular* modes, IVR occurs quickly at the above-mentioned experimental time scale. This is justified by theoretical considerations, stating that the process is greatly favoured by the huge density of the intramolecular bath coupled to the excited intramolecular levels. This is also corroborated by the dissociation of the phenol–water complex, whose surprisingly large fragmentation ratio is ascribed to the involvement of intramolecular excitation in the ion.

Finally, it should be mentioned that autoionization features could in principle perturb the 2C-DPI, since they would add discrete spikes to the fragment spectra when the photon energy matches the energy of a super-excited state of either of the molecules (M or S). Although autoionization features have been reported at very high energy levels (more than 1 eV higher than the ionization energy of molecule M), the autoionizing vibronic Rydberg features detected so far by laser experiments in Bz complexes remain weak compared with the photoionization yield (Le Calvé *et al.* 1992).

Finally, as a last example of a possible trap linked to the use of lasers, one can mention the effects of too large a laser fluence. If these fluences are such as the ion can be efficiently optically excited, the excited states of the ions formed will undergo a fast internal conversion, followed by a fast solvent evaporation, which will increase the apparent fragmentation of the complex ion. Since the ion spectroscopy can be structureless because of the short lifetime of the excited states, this unwanted additional fragmentation channel can be mistaken for the fragmentation threshold. Several anomalously low dissociation energies were obtained, for example, for Bz–ammonia (Mikami *et al.* 1988), Bz–Ar (Krause and Neusser 1992) and phenol–methanol (Mons *et al.* unpublished results). They were latter recognized as being due to optical excitation of the ion (Krause and Neusser 1993, Courty *et al.* 1998a).

*One-photon DPI.* The DPI experiment can be conducted in principle in a one-photon scheme, and historically the first measurements were actually carried out with synchrotron radiation (Grover *et al.* 1985, 1987, Walters *et al.* 1985, 1986). The lack of a first selective step, however, makes the experiment more difficult. One has actually to subtract two photoionization spectra: one obtained in presence of the two components of the complex studied and the second one in the absence of the solvent molecule, all the other parameters being kept constant. Such a procedure renders the experiment extremely difficult and does not ensure the absence of large clusters in the jet (Grover *et al.* 1988). In addition to this the one-photon scheme suffers from the same drawbacks as previously discussed (kinetic shift, bracketing effect) as well as from the poor energetic resolution of the synchrotron radiation. In addition to this, because of the lack of selectivity, the dissociation energies deduced must be corrected from the enthalpy of the complex at the jet temperature (Walters *et al.* 1985).

Nevertheless Brookhaven's group was successful on several complexes, in particular complexes of Bz (Grover *et al.* 1987, Cheng *et al.* 1995) and very interestingly of ethylene (Walters *et al.* 1986), *t*-2-butene (Grover *et al.* 1985) and 1, 3-butadiene (Grover *et al.* 1990), not readily accessible in a 2C-R2PI scheme. One must, however, notice that for a few test systems, such as Bz–water, discrepancies exist between synchrotron radiation and laser work, with apparently a significantly better precision for the latter.

## 2.2. Other techniques

Other techniques have also been developed in order to measure directly dissociation energies. They can be divided broadly into two classes.

*Vibrational predissociation of neutral complexes.* In this case one has to put enough energy in the system to cause its dissociation and one has to probe the dissociation products. A first way to do it is optical excitation, which excites vibrationally the complex in its  $S_1$  state. In the systems we discuss, which are characterized by a high density of states of intermolecular levels, two processes are *a priori* expected: either a direct predissociation mechanism or an indirect process involving first IVR and then vibrational predissociation. In both cases, dissociation will give rise to an electronically excited molecular fragment. Dissociation will be monitored by collecting the fluorescence, which is spectrally shifted relative to that of the complex. Because the technique requires an intramolecular vibrational level to be populated initially, it is currently employed for low binding energy complexes, in particular complexes of aromatic molecules with rare gas atoms (Levy *et al.* 1982, Stephenson and Rice 1984, O *et al.* 1988 and references therein).

The technique was recently refined by studying the vibrational predissociation of the electronic ground state (Bürgi *et al.* 1994). The pump-probe method used, stimulated emission pumping–resonant two-photon ionization (SEP-R2PI), consists of populating by SEP vibrationally excited levels of the complex studied and then probing a hot band of the complex by R2PI. It has been successfully applied to complexes of carbazole with polarizable atoms or molecules (Droz *et al.* 1995) as well as recently to H-bonded complexes of 1-naphthol (Bürgi *et al.* 1995, Wickleder *et al.* 1997).

These techniques usually provide a bracketing of the dissociation energy, because the density of accessible vibrational molecular levels in the dissociation range is generally low. Usually, the kinetic shift, which should be *a priori* also expected, should be much lower than in the case of ionic dissociation since the neutral well depths are much lesser.

*Photofragment kinetic measurements.* After a vibrational predissociation (in either the excited or the ionic state), the available energy flows into the several degrees of freedom of the system, and the internal energy in the photofragment is mirrored by its kinetic distribution: photofragments having the maximum kinetic energy are those formed without internal energy. Therefore the determination of the maximum energy in the kinetic distribution provides the dissociation energy desired. Using ion imaging (Heck and Chandler 1995, Yoder *et al.* 1999), a technique very sensitive to the cut-off in the kinetic distribution, since it consists in measuring a two-dimensional (2D) projection of the velocity distribution after R2PI of the  $S_1$  state fragment, a very good precision measurement ( $\pm 0.01$  kcal mol<sup>-1</sup>) of the dissociation energy of *p*-difluorobenzene–Ar has been recently published (Bellm *et al.* 2000). The feasibility of the experiment is based on the relative intensity (usually weak) of the



fragments without internal energy. Their relative intensity will probably be lower with molecular solvent molecules such as water, because of an increased density of dissociation channel states leading to (rovibrationally) excited fragments. This can render the experiment more difficult to carry out with hydrates, for instance.

### 3. Energetics of hydrogen bonding

#### 3.1. Interaction energy vs. dissociation energy

Experimental studies of the type just described measure a dissociation energy, denoted by  $D_0$ , that corresponds to the 0 K enthalpy change for the dissociation reaction (figure 4). However, this is not a measurement of the interaction energy  $D_e$ , the well depth of the complex potential energy surface, the quantity that theoreticians calculate first, since they seek the conformation of the system that minimizes the total *electronic* energy of the system.

The difference between the dissociation energy  $D_0$  and the interaction energy  $D_e$  (figure 4) is due to the change in zero-point vibrational energy ( $\Delta$  ZPE) for all the vibrations of the system resulting from the complex formation. This consists of two components: (i) the ZPE due to the six intermolecular vibrational modes of the complex ( $\text{ZPE}_{\text{inter}} = \frac{1}{2}\hbar\sum\omega_{\text{inter}}$ ) and (ii) the change in zero-point intramolecular vibrational energy of the two monomers due to the complex formation ( $\Delta$  ZPE<sub>intra</sub>).

This  $D_e - D_0$  difference can amount to 1–2 kcal mol<sup>-1</sup> for H bonds of 6–7 kcal mol<sup>-1</sup>, the intramolecular component being non-negligible, because of the significant spectral shift of the intramolecular vibrations involving the hydrogen atom engaged in the H bond. The first component can be calculated by either semi-empirical or *ab initio* calculations of the normal intermolecular modes. *Ab initio* techniques, which often carry out harmonic vibrational analysis, are not the most suitable here. Owing to the flatness and the anharmonicity of the intermolecular potential energy surface, a six-dimensional treatment usually provides a better result. Several techniques have been developed according to this approach, for example the diffusion quantum Monte Carlo technique provides the ground state level vibrational wavefunction as well as its energy in the six-dimensional well, i.e. ZPE<sub>inter</sub> (Gregory and Clary 1996, Benoit *et al.* 1998, Clary *et al.* 2000). The second component, ZPE<sub>intra</sub>, which reflects the spectral shifts of the intramolecular vibrations involving the bonding hydrogen atom, requires, however, a good description of the intramolecular force field. Therefore *ab initio* calculations are here the most relevant techniques. Because of the non-covalent nature of the complex, this contribution is usually small and negligible for very weakly bound complexes such as Bz–water (Gregory and Clary 1996) but can represent a substantial amount of total  $\Delta$  ZPE of the complex for stronger H bonds, for instance + 50% of ZPE<sub>inter</sub> in phenol–water (Schütz *et al.* 1993).

When available, the calculated  $\Delta$  ZPE has been used to provide an estimate of  $D_e$ , from the experimental  $D_0$ , which is often a safer way to evaluate it rather than to combine calculated interaction energy and  $\Delta$  ZPE. An assessment of this procedure is possible when experimental results on isotopomers of the complexes are available. Indeed, since the well depth does not depend on the masses of the nuclei, the  $D_e$  value must be independent of the isotopomer considered. This type of experiment is made possible because of the existence of a first selective step in the measurement process, whatever it is (SEP-R2PI or 2C-DPI), which makes it possible to distinguish the several isotopomers present in the jet when substitution is not complete. In

practice, however, if the isotopic shift of the electronic transition chosen is not large enough, like between indole- $\mathbf{d}_1$  and indole- $\mathbf{d}_2$ , the experiment may not be feasible (Mons *et al.* unpublished results).

Comparison of  $D_e$  values obtained by this way between light and heavy complexes has been reported so far for two species: 1-naphthol-NH<sub>3</sub> vs. 1-naphthol- $\mathbf{d}_3$ -ND<sub>3</sub> (Bürgi *et al.* 1994) and Bz- $h_6$ -H<sub>2</sub>O vs. Bz- $h_6$ -D<sub>2</sub>O (Courty *et al.* 1998b). In 1-naphthol-ammonia,  $\Delta$ ZPE, as calculated by *ab initio* methods, amounts to 1.4 kcal mol<sup>-1</sup> in the light species and 1.8 kcal mol<sup>-1</sup> in the heavy one. This leads to similar  $D_e$  values (table 1). The case of Bz-water also leads to a fairly good agreement, since the difference in ZPE<sub>inter</sub> between isotopomers has been found to remain in the same energy range, whatever the semi-empirical potential used (ZPE<sub>inter</sub>  $\sim$  0.64–0.98 kcal mol<sup>-1</sup>; substitution-induced difference,  $\sim$  0.12–0.19 kcal mol<sup>-1</sup> (Gregory and Clary 1996)). One can remark that in this case the ZPE<sub>inter</sub> has been considered with this weak complex, but a full-dimensional treatment of the intermolecular vibrations was performed because of the particular shape of the potential of this species, with its low frequencies and very anharmonic modes.

### 3.2. $\sigma$ -Type H-bonded complexes of proton donor molecules

Phenol and naphthol are both aromatic acidic molecules that form archetypal H bonds in the gas phase with proton-accepting solvent molecules. The 1:1 hydrates have been the subject of numerous UV (Gonohe 1985, Müller-Dethlefs *et al.* 1994), high-resolution UV (Berden *et al.* 1996, Helm and Neusser 1998) and IR (Tanabe *et al.* 1993, Watanabe *et al.* 1996, Matsumoto *et al.* 1998, Yoshino *et al.* 1998) laser spectroscopic studies during the last decade and the *trans*-linear hydrogen bond (figure 2(b)) is well characterized experimentally in terms of geometry, intermolecular distance and vibrational frequencies (Schütz *et al.* 1993). The energetic data were the last to be documented.

The dissociation energies of the phenol complexes with water and methanol were determined by 2C-DPI with a good precision (Courty *et al.* 1998a). The values are found in the 5–6 kcal mol<sup>-1</sup> energy range (table 1). They remain in reasonable agreement with *ab initio* calculations carried out with a medium size basis set (Schütz *et al.* 1993, Gerhards *et al.* 1994), although probably because of error compensations since values obtained with a larger basis appear to be in less agreement (Schütz *et al.* 1993). In parallel, semi-empirical models (Brenner and Millié 1994) provide a complementary insight on these gas-phase H bonds, by indicating the relative importance of the interactions at play (figure 8). Evidence is given for the major role assigned to electrostatic forces, with a significant effect of dispersion, namely the tilt of the HOC frame in methanol relative to water (Courty *et al.* 1998a, Schmitt *et al.* 2000, Kupper *et al.* 2001).

The vibrational ZPE derived from the *ab initio* calculations was used in order to provide an alternative value of the well depth  $D_e$  from the experimental  $D_0$  (table 1). Comparison between water and methanol for the  $D_e$  thus obtained suggests that these complexes have actually the *same* interaction energy and that the  $D_0$  difference essentially arises from an effect of reduced masses in their vibrations: the heavier phenol-methanol complex has smaller intermolecular vibrational frequencies and therefore a smaller ZPE<sub>inter</sub>. Such a finding, contradicting the IR spectral red shifts of the phenol OH stretch frequency ( $-\delta\nu_{\text{OH}} = 133$  and  $201$  cm<sup>-1</sup> with water and methanol respectively) makes questionable the comparisons of the bond strengths

Table 1. Compilation of experimental dissociation energies for neutral ( $D_0$ ) and ionic ( $D_0^+$ ) gas-phase hydrogen-bonded complexes of aromatic molecules, reported in the literature. An estimate (see text) of the interaction energy  $D_e$  is given when *ab initio* ZPE calculations are available. 1C-R2PI fragmentation ratios  $\tau$  are also given when available.

M	S	Type of interaction	$D_0 \pm \Delta(D_0)$ (kcal mol <sup>-1</sup> )	$D_e$ estimate	$D_0^+ \pm \Delta(D_0^+)$ (kcal mol <sup>-1</sup> )	Technique	$\tau$ (%)	References
$\sigma$ H-bonded and van der Waals complexes of proton donor molecules								
Phenol	H <sub>2</sub> O	OH—O	5.60 ± 0.11	7.4	18.54 ± 0.11	2C-DPI	15	Courty <i>et al.</i> (1998a)
	MeOH	OH—O	6.11 ± 0.18	7.4	21.40 ± 0.18	2C-DPI	8	Courty <i>et al.</i> (1998a)
	DME	OH—O	> 6.1			1C-R2PI	< 3	Mons <i>et al.</i> (unpublished results)
	NH <sub>3</sub>	OH—N	> 6.1			1C-R2PI	< 3	Mons <i>et al.</i> (unpublished results)
	CO	OH—CO	1.88 ± 0.06		6.93 ± 0.03	2C-DMATI	< 5	Haines <i>et al.</i> (1999)
	N <sub>2</sub>	OH—N <sub>2</sub>	1.24 ± 0.06		4.69 ± 0.03	2C-DMATI	< 5	Haines <i>et al.</i> (1999)
1-Naphthol	Ar	$\pi$ —Ar (dispersion)	1.04 ± 0.04		1.53 ± 0.01	2C-DMATI	< 5	Haines <i>et al.</i> (1999)
	H <sub>2</sub> O	OH—O	5.82 ± 0.20	7.4		SEP-R2PI		Bürgi <i>et al.</i> (1995)
	MeOH	OH—O	7.56 ± 0.39	8.7		SEP-R2PI		Bürgi <i>et al.</i> (1995)
	NH <sub>3</sub>	OH—N	7.66 ± 0.01	9.5		SEP-R2PI		Bürgi <i>et al.</i> (1995)
	ND <sub>3</sub>	OH—N	8.01 ± 0.04	9.4		SEP-R2PI		Bürgi <i>et al.</i> (1995)
	Benzene	OH— $\pi$	5.08 ± 0.06			SEP-R2PI		Wickleder <i>et al.</i> (1997)
Indole	C <sub>6</sub> H <sub>12</sub>	Dispersion	6.92 ± 0.04			SEP-R2PI		Wickleder <i>et al.</i> (1997)
	Oxirane	OH—O	7.72 ± 0.13			SEP-R2PI		Wickleder <i>et al.</i> (1997)
	H <sub>2</sub> O	> NH—O	4.84 ± 0.23	6.2	13.88 ± 0.25	2C-DPI	55	Mons <i>et al.</i> (1999)
	H <sub>2</sub> O	> NH—O	4.67 ± 0.04	6.1	13.70 ± 0.03	2C-DMATI		Braun <i>et al.</i> (1998)
	MeOH	> NH—O	5.60 ± 0.37		14.64 ± 0.44	2C-DPI		Mons <i>et al.</i> (unpublished results)
	Benzene	> NH— $\pi$	5.21 ± 0.04		13.10 ± 0.03	2C-DMATI		Braun <i>et al.</i> (1998)
Formanilide	Ar	Dispersion	1.29 ± 0.04		1.54 ± 0.03	2C-DMATI		Braun <i>et al.</i> (1998)
	H <sub>2</sub> O	> NH—O	5.65 ± 0.30	7.0		2C-DPI	22	Mons <i>et al.</i> (2001)
$\sigma$ H-bonded complexes of proton-accepting molecules								
Anisole	H <sub>2</sub> O	> O—HOH	3.69 ± 0.11		—	2C-DPI	95	Mons <i>et al.</i> (unpublished results)
	H <sub>2</sub> O	> CO—HOH	5.4 ± 0.3	7.2	—	2C-DPI	47	Mons <i>et al.</i> (2001)
<i>p</i> -Difluorobz	H <sub>2</sub> O	F—HOH	2.79 ± 0.03		—	2C-DPI		Brenner <i>et al.</i> (1995)

$\pi$ H-bonded and van der Waals complexes of proton-accepting molecules					
Benzene	$\pi$ -HOH	$1.6 < D_0 < 4.2$			Gord <i>et al.</i> (1990)
H <sub>2</sub> O	$\pi$ -HOH	$1.63 < D_0 < 2.78$			Gotch and Zwiier (1992)
H <sub>2</sub> O	$\pi$ -HOH	$2.25 \pm 0.28$			Cheng <i>et al.</i> (1995)
H <sub>2</sub> O	$\pi$ -HOH	$2.44 \pm 0.09$	3.2		Courty <i>et al.</i> (1998b)
D <sub>2</sub> O	$\pi$ -DOD	$2.67 \pm 0.11$	3.3		Courty <i>et al.</i> (1998b)
NH <sub>3</sub>	$\pi$ -HNH <sub>2</sub>	$1.84 \pm 0.11$			Mons <i>et al.</i> (unpublished results)
HCl	$\pi$ -HCl	$1.8 < D_0 < 3.8$			Gord <i>et al.</i> (1990)
HCl	$\pi$ -HCl	$4.79 \pm 0.12$			Walters <i>et al.</i> (1985)
HCl	$\pi$ -HCl	$2.90^a \pm 0.50$			Walters <i>et al.</i> (1985)
CH <sub>3</sub> Cl	Dispersion	$1.5 < D_0 < 3.4$			Gord <i>et al.</i> (1990)
CHCl <sub>3</sub>	Dispersion	$2.0 < D_0 < 4.6$			Gord <i>et al.</i> (1990)
CCl <sub>4</sub>	Dispersion	$2.4 < D_0 < 3.2$			Gord <i>et al.</i> (1990)
O <sub>2</sub>	Dispersion	$1.65 \pm 0.32$			Grover <i>et al.</i> (1992)
SO <sub>2</sub>	Dispersion-electrostatic	$4.40 \pm 0.28$			Grover <i>et al.</i> (1985)
Benzene	Dispersion-electrostatic	$1.61 \pm 0.23$	1.9		Ernstberger <i>et al.</i> (1990)
Benzene	Dispersion-electrostatic	$1.66 \pm 0.23$	2.0		Courty <i>et al.</i> (1998a)
Benzene	Dispersion-electrostatic	$2.40 \pm 0.40$			Grover <i>et al.</i> (1987)
Ar	$\pi$ -Ar (dispersion)	$< 0.97$		$< 1.46$	Krause and Neusser (1993)
C <sub>6</sub> F <sub>6</sub>	$\pi$ -DOD	$2.10 \pm 0.40$			Grover <i>et al.</i> (1992)
Anthracene	$\pi$ -HOH	$3.15 \pm 0.60$			Palmer and Topp (1998)
Perylene	Dispersion-electrostatic	$< 3.53$			Topp (1993)
	Dispersion-electrostatic	$1.78 < D_0 < 2.30$			Topp (1993)
1Me-indole	$\pi$ -HOH	$4.10 \pm 0.14$	5.7		Mons <i>et al.</i> (1999)
C <sub>2</sub> H <sub>4</sub>	$\pi$ -HOH	$< 3.18 \pm 0.74$			Walters <i>et al.</i> (1986)

<sup>a</sup>Data reinterpreted (see text).

from the IR data. With dimethylether (Courty *et al.* 1998a) and ammonia (Mons *et al.* unpublished results), the experiment could not be carried out because of the too small fragmentation ratio of these species. This suggests that the binding energy of the phenol<sup>+</sup> cation to these better proton acceptors is much larger than with water or methanol.

Comparison can also be made with van der Waals complexes of phenol with Ar, N<sub>2</sub> or CO (Haines 1999). The neutral dissociation energies found, all in the 1–2 kcal mol<sup>-1</sup> range, feature the dominant role of dispersive interactions. The ionic dissociation energy remains in the kcal mol<sup>-1</sup> range for Ar. It jumps to the 4–7 kcal mol<sup>-1</sup> region for the more polarizable N<sub>2</sub> and CO molecules, but is still 3–4 times smaller than with the dipolar species (water and methanol): *ca.* 20 kcal mol<sup>-1</sup>.

The dissociation energy of the 1-naphthol complexes with several solvent molecules was experimentally bracketed using the SEP-R2PI technique (Bürgi *et al.* 1995, Wickleder *et al.* 1997). With water, the same order of magnitude to phenol is found for both  $D_0$  and  $D_e$ , illustrating the similar strengths of the H bonds, in particular an interaction energy of 7.4 kcal mol<sup>-1</sup>. The 1-naphthol–methanol complex seems to deviate from the series, with a large value, similar to that found with ammonia (7.66 kcal mol<sup>-1</sup>), a much stronger acceptor. *Ab initio* calculations (second-order Møller–Plesset (MP2) with basis set superposition error (BSSE) correction on self-consistent field (SCF) optimized geometries) do seem to reach a good agreement with experiment, apart from naphthol–methanol whose experimental value seems again to be overestimated by about 1 kcal mol<sup>-1</sup>. With Bz, a lower binding energy is found (5 kcal mol<sup>-1</sup>), according to the weaker proton affinity of the  $\pi$  ring.

Indole also gives rise to a H-bonded complex via its NH moiety, with a type of interaction (figure 8) similar to that of phenol–water (Korter *et al.* 1998).  $D_0$  was measured by MATI on the complexes of indole with water and Bz (Braun *et al.* 1998). The value for indole–water is in fair agreement with the 2C-DPI experiment (Mons *et al.* 1999). Recent *ab initio* calculations ( $D_0 = 4.45$  kcal mol<sup>-1</sup>;  $D_e = 5.80$  kcal mol<sup>-1</sup> (van Mourik *et al.* 2000)) indicate that large basis sets

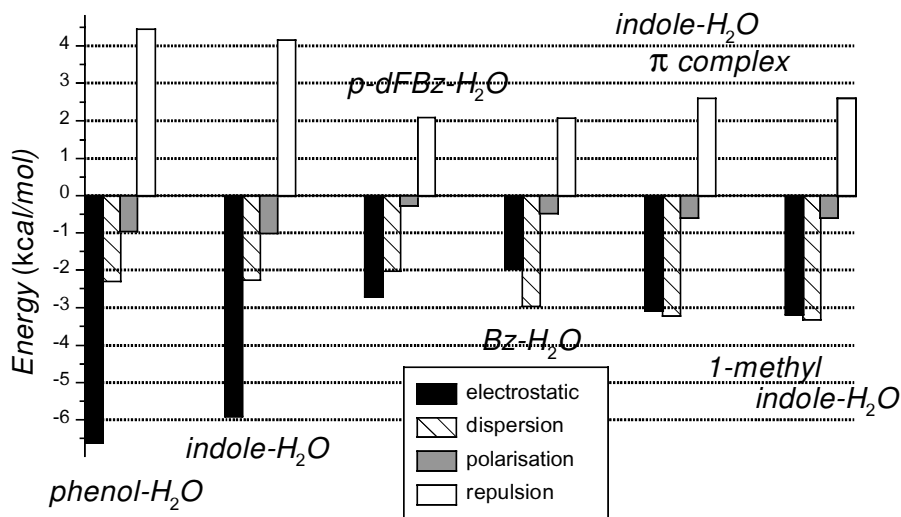


Figure 8. Components of the interaction energy (kcal mol<sup>-1</sup>) of several minima of H-bonded complexes as obtained from the semi-empirical model of Brenner and Millié (1994).

(complete Dunning's basis set limit) and high levels of theory (MP2 or CCSD(T)) are required to meet the experimental values within  $0.3 \text{ kcal mol}^{-1}$ . The methanol complex is found to have a binding energy slightly larger than the hydrate, similarly to the phenol complexes (Mons *et al.* unpublished results). The Bz complex is as bound as the methanol complex, which suggests that the lesser accepting character of Bz is compensated for by the increased dispersive interaction, due to the high polarizability of Bz.

Although not being, strictly speaking, in the scope of the present review on H-bonded complexes, it is worth mentioning that dissociation energies of complexes of aromatic molecules with argon have also been obtained during the last decade. The rare gas atom is generally located above the Bz ring in all these complexes (Leutwyler and Jortner 1987, Leutwyler and Bösiger 1990) and a good agreement is reached nowadays for the aromatic–Ar dissociation energies with values spanning from *ca.*  $1 \text{ kcal mol}^{-1}$  for monocyclic aromatic molecules ( $< 0.972 \text{ kcal mol}^{-1}$  for Bz–Ar (Krause and Neusser 1993);  $0.917 \text{ kcal mol}^{-1}$  for fluorobenzene–Ar (Grebner *et al.* 1997)) up to  $1.5 \text{ kcal mol}^{-1}$  for larger aromatics with enhanced dispersion forces ( $1.44 \text{ kcal mol}^{-1}$  for dibenzo- $\pi$ -dioxin (Grebner and Neusser 1995),  $1.517 \text{ kcal mol}^{-1}$  for carbazole (Bürgi *et al.* 1994)). This field has recently been reviewed by Haas and Kandler (1997). The dissociation energies of these species bound by dispersion forces are typically 4 times less than that of the H-bonded phenol–water complex.

### 3.3. $\pi$ -Type H-bonded complexes

Evidence for the existence of gas-phase complexes with a  $\pi$  system playing the role of a proton acceptor has been obtained from IR (Zwier 1996) and rotational (Legon and Millen 1986, Suzuki *et al.* 1992, Rodham *et al.* 1993) spectroscopy. These so-called  $\pi$ -type hydrogen bonds constitute a real challenge to the theoreticians because of the large dispersive character of the interaction at play in these systems. Density functional theory (DFT) will generally fail to describe properly the interaction and, alternatively, high levels of theory together with extended basis sets are required in the alternative *ab initio* calculations (Dunning 2000, Kim *et al.* 2000, Rappé and Bernstein 2000).

#### 3.3.1. Bz–H<sub>2</sub>O

This archetypal system is probably the most documented so far because of its simplicity, its symmetry, the interest of the water– $\pi$  interaction for biology and, from a theoretical point of view, for the challenge it represents.

There is strong evidence, from rotational spectroscopy (Suzuki *et al.* 1992, Gutowski *et al.* 1993), for the location of the O atom of water on the C<sub>6</sub> axis of Bz (figure 3(b)), as well as from IR spectroscopy (Pribble *et al.* 1995), for nearly free rotation of water in the complex. Calculated structures (see the review by Kim *et al.* (2000) for more details) confirm the location of the O atom and provide evidence for a very shallow potential along the coordinate of rotation of the water molecule in its plane: depending on the basis chosen, the complex is found to be mono- or double dentate, with one or both H atoms of water pointing to the ring. This is probably the manifestation of a subtle balance between electrostatics and dispersive interactions.

The photoionization curve of the complex has already been discussed (figure 3(a)). The first DPI measurements made by Grover and coworkers (Cheng *et al.* 1995) are in agreement with the earlier bracketing by Gotch and Zwier (1992) using the dispersed fluorescence technique. The later laser 2C-DPI measurement by Courty

Table 2. Comparison between recent theoretical and experimental data on the energetics of Bz-H<sub>2</sub>O.

	<i>Ab initio</i> calculations			Experimental data		
	Kim <i>et al.</i> (1997)	Feller (1999)	Tsuzuki <i>et al.</i> (2000)	Courty <i>et al.</i> (1998a)	Cheng <i>et al.</i> (1995)	Gotch and Zwier (1992)
$D_e$ (kcal mol <sup>-1</sup> )	3.77 ± 0.68	3.9 ± 0.2	3.17 <sup>a</sup>			
$D_0$ (kcal mol <sup>-1</sup> )	2.74 ± 0.68	2.9 ± 0.2	2.17 <sup>a,b</sup>	2.44 ± 0.09	2.25 ± 0.28	1.63–2.78

<sup>a</sup> Intermolecular distance not fully optimized.

<sup>b</sup> Assuming the same ZPE as Feller (1999).

*et al.* (1998b) improved Cheng's measurement by a factor of 3, yielding the most accurate value: 2.44 ± 0.09 kcal mol<sup>-1</sup>.

The most recent calculations (Feller 1999, Tsuzuki *et al.* 2000) have shown that reasonable agreement with experiment can be met when very large basis sets are used. Basis set superposition error BSSE correction tends to decrease but still represents 15% of the interaction energy for basis sets as large as aug-cc-VQZ. Values close to the complete basis set limit (typically 0.3 kcal mol<sup>-1</sup>) can be obtained with this basis set size. Similar values are also observed for the two treatments of correlation (MP2 and CCSD(T)), with slightly smaller binding energy values (0.3 kcal mol<sup>-1</sup>) observed for the coupled-cluster approach. Taking into account these trends, several values were proposed (table 2).

A reasonable agreement is obtained between *ab initio* calculations and experiment. In addition, semi-empirical models (Brenner and Millié 1994) unravel the very different nature of the  $\pi$ -type H bonds compared with the conventional ones (figure 8), with dispersion as the dominant attractive interaction. Obviously, in such a case, calculation strategies involving geometry optimization at the SCF level would fail.

### 3.3.2. Bz-NH<sub>3</sub>

The complex structure is known from rotational spectroscopy, which provides evidence for a  $\pi$ -type structure and a nearly free internal rotation of NH<sub>3</sub> (Rodham *et al.* 1993). More precisely, recent calculations (figure 9(a)) suggest a monodentate H bonding structure (Tsuzuki *et al.* 2000). The dissociation energy was estimated from the rotational analysis of the spectra: the combination of the rotational distortion constant with a model assuming the shape of the van der Waals potential yielded a value of 1.4 kcal mol<sup>-1</sup> (Rodham *et al.* 1993). The direct energetics measurement carried out in our group used the 2C-DPI technique (Mons *et al.* unpublished results). As for all the  $\pi$ -type systems, a large fragmentation ratio is expected and indeed observed. Because of a strong pollution of the experiment by the Bz clusters, an unusual strategy was used: instead of monitoring the fragmentation ratio, the information related to the fragmentation threshold was taken from the parent photoion yield curve alone, i.e. from the onset of its plateau (saturation: see figure 9). The edge of this plateau allows us to provide a measurement of the dissociation energy,  $D_0 = 1.84 \pm 0.11$  kcal mol<sup>-1</sup>, significantly larger than that deduced from the rotational distortion constant, illustrating the too large sensitivity of this type of estimate to the potential shape. The Bz-ammonia complex is less

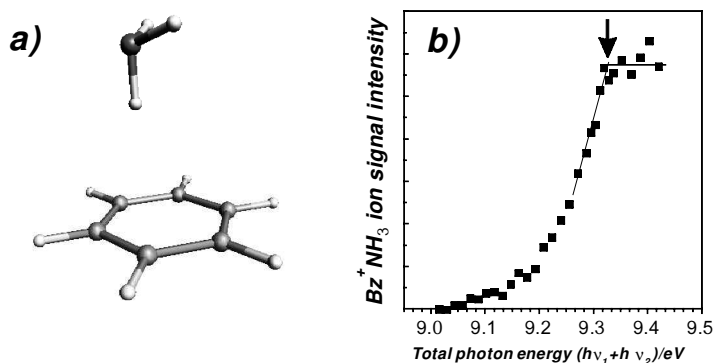


Figure 9. Benzene–NH<sub>3</sub> complex: (a) minimum energy conformation of the neutral complex, as obtained by a semi-empirical model (Brenner and Millié 1994), (b) photoionization curve as obtained by two-colour R2PI, showing the saturation of the complex ion beyond the dissociation threshold, indicated by an arrow (Mons *et al.* unpublished results).

strongly bound than the water complex by more than 0.5 kcal mol<sup>-1</sup>. This is partially due to the lower electrostatics interaction compared with dispersion, as illustrated by our semi-empirical model (Mons *et al.* 2001). A fair agreement is found between the present experimental data and the best *ab initio* calculations of the literature (see table 3).

The large dissociation ratio in the 1C-R2PI experiment together with the slowly rising photoionization threshold suggests again, as in the model case of Bz–water, that the ion possesses a very different equilibrium structure, with a flipped-over ammonia molecule which optimizes the charge–dipole interaction.

### 3.3.3. Bz–HCl

As with water, the key to the structure is given by microwave spectroscopy (Read *et al.* 1981, 1983) with an equilibrium geometry similar to that of Bz–H<sub>2</sub>O: with the H atom of HCl pointing to the Bz ring. From the rotational data analysis, very different interaction energies (5.5 or 2.1 kcal mol<sup>-1</sup>) were also obtained, depending on the potential shape chosen for the model. Concerning photoionization, a non-adiabatic behaviour and a large fragmentation ratio are also expected for this species.

Table 3. Comparison between recent theoretical and experimental data on the energetics of Bz–NH<sub>3</sub>.

	<i>Ab initio</i>		Experimental: Mons <i>et al.</i> (unpublished work)
	Tsuzuki <i>et al.</i> (2000)	Tarakeshwar <i>et al.</i> (2001)	
	CCSD(T) basis set limit; MP2 basis set limit plus CCSD(T) correction term; geometry partially optimized	MP2/aug-cc-pVDZ; partially (50%) BSSE corrected	
$D_e$ (kcal mol <sup>-1</sup> )	2.22	3.21	
$D_0$ (kcal mol <sup>-1</sup> )	1.61 <sup>a</sup>	2.13	1.84 ± 0.12

<sup>a</sup> ZPE evaluated at the MP2/cc-pVTZ level.



Only two sets of direct energetic measurements exist on the complex. The dissociation energy bracketing obtained by Gotch and Zwier (1992) by analysing the dispersed fluorescence yields:  $1.8 \text{ kcal mol}^{-1} \leq D_0 \leq 3.8 \text{ kcal mol}^{-1}$ . This is in disagreement with the value obtained by Grover and coworkers (Walters *et al.* 1985) derived from a 1P-DPI experiment:  $4.79 \pm 0.12 \text{ kcal mol}^{-1}$ . Such a large discrepancy deserves attention. A critical reading of the latter paper points out the likely presence of large clusters in this experiment. The absence of large cluster ions, invoked by the authors, is unfortunately not sufficient to rule out their presence in the expansion because of fragmentation expected for these species, similar to the Bz–water clusters. The  $\text{Bz}^+\text{–HCl}$  ion channel is therefore probably widely polluted by fragmentation products from larger clusters, inasmuch as pure HCl was used for the expansion. Good evidence for this extensive fragmentation is seen in the shape of the  $\text{Bz}^+\text{–HCl}$  ion yield curve they observe. As discussed before, for a complex of this type with unfavourable photoionization FC factors, one has to expect a slowly increasing parent ion signal followed by a saturation when the photon energy overcomes the ionic dissociation limit, as already shown for Bz–water and Bz– $\text{NH}_3$  in figures 3(b) and 9(b). The  $\text{Bz}^+\text{–HCl}$  ion yield found by Walters and coworkers indeed does reach a weak intensity plateau and afterwards increases dramatically. The onset of this increase does correspond to a well-defined onset of the  $\text{Bz}^+$  ion. This seems consistent with the fact that large clusters can lose more than one HCl molecule. Under the conditions of the experiment, the amount of clusters was probably so large that it masked the dissociation of the  $\text{Bz}^+\text{–HCl}$  ions into the  $\text{Bz}^+$  mass channel. So that, instead of choosing the intense onset of the  $\text{Bz}^+$  mass channel to measure the dissociation energy of Bz–HCl, we interpret the weak plateau as the saturation of the  $\text{Bz}^+\text{–HCl}$  ion at its dissociation limit. Instead of the value reported by Walters *et al.* (1985), we derive a much lower value ( $D_0 = 2.90 \pm 0.50 \text{ kcal mol}^{-1}$ ), that is in agreement with the bracketing of Gotch and Zwier (1992).

Interestingly, only sparse *ab initio* data are available. Kim *et al.* (2000) provide in their review a comparison of the HCl and water complexes carried out at two degrees of theory (MP2/6-31+G\* and MP2/6-311++G(3df,2p)//MP2/6-311++G\*\*). Owing to the large BSSE obtained as well as the trend of the BSSE correction to be overestimated (Kim *et al.* 1997), the authors provide  $D_e$  values of  $4.0 \pm 1.5$  and  $5.5 \pm 1.2 \text{ kcal mol}^{-1}$  for Bz–HCl, depending on the basis used. The corresponding dissociation energies  $D_0$ , in the  $3.0 \pm 1.5$  and  $4.5 \pm 1.2 \text{ kcal mol}^{-1}$  ranges, lie between 1.0 and  $1.8 \text{ kcal mol}^{-1}$  higher than that found for Bz– $\text{H}_2\text{O}$ , which seems to be surprising considering the smaller dipole moment of HCl (1.1 D vs. 1.8 D for water).

According to this theoretical comparison between Bz– $\text{H}_2\text{O}$  and Bz–HCl and taking our experimental energy of Bz– $\text{H}_2\text{O}$  ( $2.44 \text{ kcal mol}^{-1}$ ) as a reference, one obtains an alternative  $D_0$  estimate for HCl lying between 3.4 and  $4.2 \text{ kcal mol}^{-1}$ , which is in agreement neither with the value obtained by Walters *et al.* (1985) nor with the value deduced from the above-mentioned analysis of their data. The question is still open and this is a nice example of what 2C-DPI experiments can bring to the field, owing to the real difficulties encountered by theoreticians for these systems.

### 3.3.4. Other complexes

Other complexes of Bz have also been investigated by Grover, Walters and coworkers by one-photon DPI and the corresponding dissociation energies derived.

Although not being H bonded, the Bz dimer, because of its archetypal nature, deserves discussion. Its photoionization was investigated some years ago (Grover *et al.* 1987). The authors emphasize the absence of autoionization features but do not comment on the clearly non-adiabatic slowly rising photoionization threshold. They nevertheless used the apparent ionization energy, implicitly assumed as adiabatic, in combination with the best value of the dissociation energy of the ionic complex, derived from a compilation of various experimental sources, including high-pressure mass spectrometry and photodissociation, to propose a value of  $2.4 \pm 0.4 \text{ kcal mol}^{-1}$ , for the neutral dimer according to relation (3). However, because of the non-adiabatic nature of the ionization energy measured for the complex,  $D_0$  was overestimated. After a first laser study of the system (Börnson *et al.* 1988) that yielded a higher ionization energy, a dispute between the representatives of the synchrotron radiation (Grover *et al.* 1989) and laser (Selzle *et al.* 1989) communities took place, about the nature of photoionization threshold. The final answer was given by Selzle *et al.* who showed that a delayed ionization in a two-colour experiment led to a lower ionization energy value, because of a more extensive exploration of the intermolecular potential energy surface taking place in the  $S_1$  state. Unfortunately the consequence for the binding energy value given by Grover *et al.* (1987) was not given. Finally, reliable values arrived with the two-colour laser DPI measurements (Ernstberger *et al.* 1990, Courty *et al.* 1998b), which lead to a value close to  $1.63 \pm 0.23 \text{ kcal mol}^{-1}$  for the most populated isomer among the two species shown to coexist in the jet (Scherzer *et al.* 1992). The most recent calculations at a high level of theory (correlation at the CCSD(T) level) (Hobza *et al.* 1996) confirm the existence of two minima on the neutral potential energy surface, with similar stabilization energies:  $2.3 \text{ kcal mol}^{-1}$  for the T-shaped structure and  $2.15 \text{ kcal mol}^{-1}$  for a parallel-displaced conformation. Combined with ZPE corrections ( $0.3 \text{ kcal mol}^{-1}$  Hobza *et al.* 1994), a dissociation energy of  $\sim 1.9 \text{ kcal mol}^{-1}$  is deduced in fair agreement with experiment. The range of accuracy now obtained experimentally, for instance using the MATI technique, should probably provide a reliable determination of the relative stability of the Bz dimers and therefore assess the capability of high level *ab initio* calculations to predict correctly the energetics of regions of the intermolecular energy surface that are controlled by interactions of different types.

It is worthwhile to note the binding energies determined in the 1P-DPI for the complexes of Bz with  $\text{SO}_2$  (Grover *et al.* 1985) and  $\text{O}_2$  (Grover *et al.* 1992). The permanent dipole of  $\text{SO}_2$  leads to an energetic range of  $4 \text{ kcal mol}^{-1}$ , whereas with the  $\text{O}_2$  molecule it drops to  $1.6 \text{ kcal mol}^{-1}$ .

Other  $\pi$ -bound complexes of ethylene, 1,3-butadiene and *trans*-2-butene, were also investigated by the same group. Complexes of 1,3-butadiene and *trans*-2-butene with  $\text{SO}_2$  (Grover *et al.* 1985, 1990) were found to be in the 3–4  $\text{kcal mol}^{-1}$  energy range, i.e. with slightly smaller binding energies than with Bz. The same trend is found for ethylene–HCl, for which an upper bound of  $3.2 \text{ kcal mol}^{-1}$  is given (Walters *et al.* 1986).

### 3.3.5. Other aromatic molecules

The case of the *para*-difluorobenzene (*pdFB*) molecule allows us to evaluate the effect of the fluorine atom. Originally studied for its ionic reactivity (Brutschy 1992), the *pdFB*– $\text{H}_2\text{O}$  complex was found to have its water molecule in the equatorial plane, with one of the H atoms pointing to the fluorine (Brenner *et al.* 1995,

Tarakeshwar *et al.* 1999). The dissociation energy was found to be significantly larger (by  $0.35 \text{ kcal mol}^{-1}$ ) than that of Bz–water. The decomposition of the interaction into its components as given by a semi-empirical model (figure 8) shows that the qualitative structural difference between *pdFB*– $\text{H}_2\text{O}$  and Bz– $\text{H}_2\text{O}$  is also reflected in the reversed trend of the main attractive interactions at play: dispersion is less intense in *pdFB*– $\text{H}_2\text{O}$  but electrostatics is larger. In this respect, *pdFB*– $\text{H}_2\text{O}$  is closer to phenol– $\text{H}_2\text{O}$ , with, however, a much lower electrostatic component.

Energetic data on complexes of larger aromatic molecules are rather sparse although the dynamics and the spectroscopy of molecules such as carbazole, perylene and anthracene have been extensively studied (Leutwyler and Jortner 1987, Leutwyler and Bösigler 1990, Topp 1993, Palmer and Topp 1998). Dissociation energies of van der Waals complexes of perylene bound by dispersive interactions such as perylene– $\text{CO}_2$  ( $D_0 < 3.53 \text{ kcal mol}^{-1}$ ) or perylene–methane ( $1.78 \text{ kcal mol}^{-1} < D_0 < 2.30 \text{ kcal mol}^{-1}$ ) have been bracketed by dispersed fluorescence (Topp 1993, Wittmeyer and Topp 1993). The spectroscopy of anthracene complexes with water was investigated by 2C-R2PI and the energetic window leading to stable ions as well (Palmer and Topp 1998). Combining these data allows us to estimate the dissociation energy of anthracene– $\text{H}_2\text{O}$  to be  $3.15 \pm 0.60 \text{ kcal mol}^{-1}$ , which is more bound than the complex of Bz, in agreement with the large dispersive interaction and the larger polarizability of anthracene.

### 3.4. Towards a mapping of the intermolecular PES of H-bonded complexes

Formation of 1:1 complexes in a supersonic expansion leads generally to the most stable structure although the solute and solvent molecule can exhibit both proton acceptor and donor sites and therefore several complex conformations can *a priori* be expected. As an example, besides the OH donor group, phenol presents two acceptor sites: the lone pairs on the oxygen atom as well as the  $\pi$  ring. A similar situation is expected for the indole hydrates: in addition to the  $\sigma$ –H bond, a  $\pi$ -bonded (similar to Bz– $\text{H}_2\text{O}$ ) complex could exist. However, only one hydrate is observed in supersonic jets, namely that corresponding to the phenol and indole donor H bonds, which suggests that the barrier(s) between the minima can easily be crossed during the cooling processes in the early stages of the expansion or that the secondary site is not a minimum.

This is a quite common behaviour, for which there are only a few exceptions, generally encountered with large molecules with well-separated sites for a small protic solvent molecule: one can mention, for example, the two conformers of *trans*-N-phenylformamide (or formanilide) with water (Dickinson *et al.* 1999, Robertson 2000, Fedorov and Cable 2000), the three complexes of *para*-chlorofluorobenzene (*pClFBz*) with  $\text{CH}_3\text{OH}$  (Riehn *et al.* 2000) and the conformers of methyl-*p*-aminobenzoate– $\text{H}_2\text{O}$  (Longarte *et al.* 2000), even if in this last case the IR spectroscopy is still to be done to strengthen the size assignment. The case of the two conformations of Bz<sub>2</sub> would also deserve mention in this discussion although no H bond is at play in this system.

Among these species, special attention has been recently focused on the hydrates of *trans*-formanilide, because of their potential relevance to biology: the molecule indeed presents an amide group that mimics the peptide bond. Taking advantage of the knowledge of the spectroscopy of these complexes (figure 5), dissociation energies of the two monohydrates were measured by 2C-DPI (Mons *et al.* 2001) and were found to be the same ( $\sim 5.5 \text{ kcal mol}^{-1}$ ) within the precision of the

experiment. This result, in agreement with the coexistence of the two species in the jet, pleasingly confirms the reliability of the energetic measurements. Similar experiments would be interesting for the other cases cited above, since they constitute a precise test for calculations, which generally encounter difficulties in computing H bonds of different nature with the same degree of accuracy (Hobza *et al.* 1996, Carney and Zwier 1999, Tarakeshwar *et al.* 1999, Riehn *et al.* 2000).

In order to evaluate the energetics of secondary hydration sites, not observed experimentally, our group has sought to compare these secondary sites with the hydrate of a methyl-substituted molecule, in which the formation of the primary site is forbidden (figure 10). This strategy proved to be successful for phenol and indole, since their secondary site was evaluated experimentally from the hydrate of anisole (methoxyBz) and 1-methyl indole respectively. With indole, this approach was validated by semi-empirical calculations that provided evidence for similar geometry and energetics within both systems (Mons *et al.* 1999). Figure 8, with the components of the total energy as obtained from this model, illustrates the same interactions at play in both species. This was confirmed recently by MP2 calculations at the complete basis set limit (van Mourik *et al.* 2000), in contrast to the DFT method that does not account properly for the dispersion interaction (table 4).

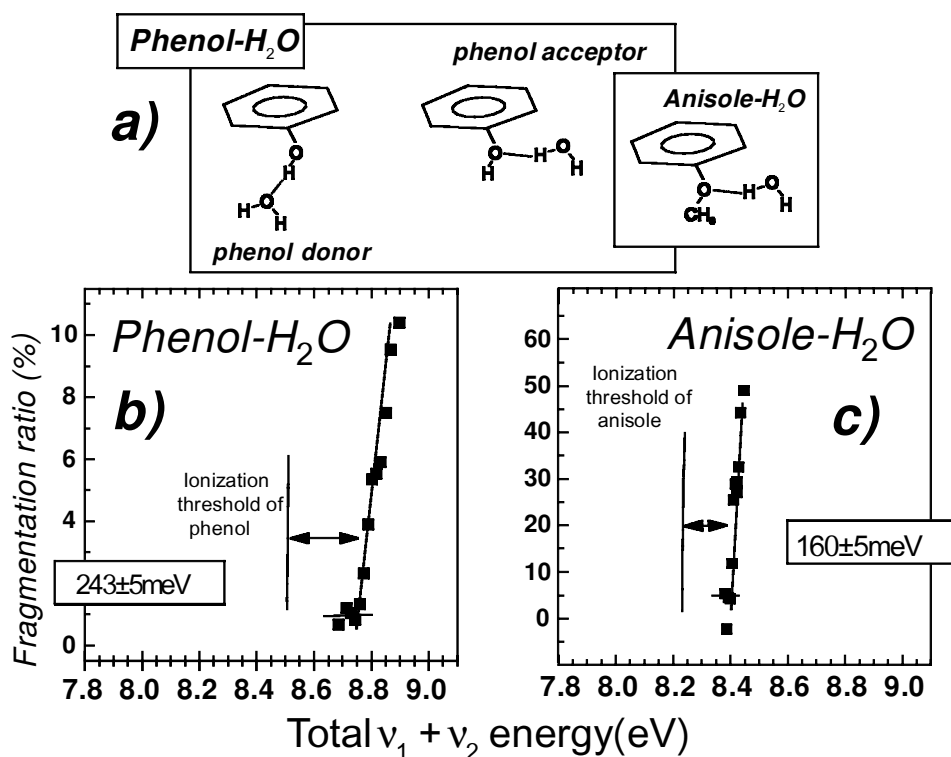


Figure 10. (a) The two main conformers of the phenol-H<sub>2</sub>O complex, with phenol acting as either a proton donor or an acceptor, and the anisole-water complex. (b) Fragmentation ratio of the phenol-H<sub>2</sub>O complex as a function of the two-photon energy (Courty *et al.* 1998b). (c) Fragmentation ratio of the anisole-H<sub>2</sub>O complex as a function of the two-photon energy (Mons *et al.* unpublished results).

Table 4. Comparison between recent theoretical and experimental data on the energetics of the  $\sigma$  and  $\pi$ -bound 1:1 hydrates of indole and 1-methyl indole.

Structure	Method	References	$D_e$ (kcal mol <sup>-1</sup> )	$D_0$ (kcal mol <sup>-1</sup> )
Indole-H <sub>2</sub> O $\sigma$ complex	MP2/complete basis set limit	van Mourik <i>et al.</i> (2000)	5.80	4.44
	B3LYP/6-31+G*	Carney and Zwier (1999)	5.05	3.63
	Semi-empirical	Mons <i>et al.</i> (1999)	4.99	3.56
	Semi-empirical	Carles <i>et al.</i> (2000)	6.34	
	Experimental	Braun <i>et al.</i> (1998)		4.84
Indole-H <sub>2</sub> O $\pi$ complex	Experimental	Mons <i>et al.</i> (1999)		4.66
	MP2/complete basis set limit	van Mourik <i>et al.</i> (2000)	5.07	3.61
	B3LYP/6-31+G*	Carney and Zwier (1999)	3.76 <sup>a</sup>	2.60 <sup>a</sup>
1-methyl indole-H <sub>2</sub> O $\pi$ complex	Semi-empirical	Mons <i>et al.</i> (1999)	4.27	
	MP2/complete basis set limit	van Mourik <i>et al.</i> (2000)	5.85	4.28
	B3LYP/6-31+G*	Carney and Zwier (1999)	2.87	1.65
	Semi-empirical	Mons <i>et al.</i> (1999)	4.47	3.27
	Experimental	Mons <i>et al.</i> (1999)		4.10

<sup>a</sup>Not corrected for BSSE.

The anisole–water complex (figure 10), whose structure has been confirmed experimentally by IR–UV double-resonance spectroscopy (Barth *et al.* 1998), provides an interesting evaluation of the second site of phenol–water ( $3.69 \text{ kcal mol}^{-1}$ ). This value is much lower than the main site ( $5.6 \text{ kcal mol}^{-1}$ ), which argues in favour of an efficient relaxation toward the most stable conformer during the expansion. The interest of this system also resides in its similarity to the water dimer. Indeed, no direct  $D_0$  measurement exists for the latter species. In particular, the DPI technique cannot work here because of the proton transfer reaction occurring in the ion (Ng *et al.* 1977). A  $D_e$  value ( $5.44 \pm 0.7 \text{ kcal mol}^{-1}$ ) was extrapolated 20 years ago from the 373 K association enthalpy measurement based on the conductivity of the water vapour, relying on a ‘significant amount of interpretation and on the use of theoretical models’ (Curtiss *et al.* 1979). In counterpart the best complete basis set *ab initio* calculations have led to the best estimate of  $D_e = 5.0 \pm 0.1 \text{ kcal mol}^{-1}$  and then to  $D_0 = 3.1 \pm 0.2 \text{ kcal mol}^{-1}$  (Mas and Szalewicz 1996, Feyereisen *et al.* 1996, Halkier *et al.* 1997, Xantheas 1996). Pleasingly, the value found for the 1:1 anisole hydrate is very close to this range, although slightly larger.

### 3.5. Energetics of larger complexes

Larger and more complex systems have been recently investigated. Flexible molecules have received particular attention (Brutschy 2000, Desfrancois *et al.* 2000, Robertson and Simons 2001). UV and IR–UV spectroscopies are used to investigate the conformational landscape of these species as well as their hydrates. Experimental efforts, using R2PI, have been worked out on the spectroscopy and the energetics of H-bonded complexes of chiral molecules, such as 1-phenyl-ethanol (Giardini Guidoni *et al.* 2000, Mons *et al.* 2000a) and 1-phenyl-propanol (Latini *et al.* 2000, Satta *et al.* 2000), with chiral solvent molecules such as 2-butanol. The motivation is then to shed some light on the nature of the intermolecular forces at play in the chiral discrimination, for instance by comparing the spectroscopy and the energetics of diastereoisomeric complexes (*RR* and *SS* on the one hand, *RS* and *SR* on the other hand) (Al-Rabaa *et al.* 1997). In the case of flexible molecules, however, it has been shown that several effects work together to make life more complicated to the spectroscopists. First, the floppy molecules themselves present a non-adiabatic photoionization threshold, essentially because the floppiness of their tail allows the molecule to adapt its geometry to the interaction change between neutral and ionic states, as clearly shown recently by laser photoelectron studies (Dessent *et al.* 2000, Weinkauff *et al.* 2000). As a consequence the dissociation energies derived from these 2C-DPI studies yield only a lower limit of  $D_0$ , even if this feature is not always pointed out in the reports. For instance this property precludes unfortunately any precise measurement on hydrates of biomimetic molecules, whose spectroscopy has been studied recently, such as phenylethylamine (Sun and Bernstein 1996, Hockridge and Robertson 1999, Yao *et al.* 2000), benzyl alcohol (Mons *et al.* 2000a) and 2-phenyl-ethanol (Robertson and Simons 2001).

Nevertheless, these experiments can in principle derive the *relative* stability of two diastereoisomeric complexes for example. Such values were recently obtained on H-bonded complexes of chiral alcohol molecules (Latini *et al.* 2000, Mons *et al.* 2000a). As an example, the homochiral complex (*R*)1-phenyl-ethanol–(*R*)2-butanol is found to be more stable than the hetero complex (*R*)1-phenyl-ethanol–(*S*)2-butanol by *ca.*  $0.7 \text{ kcal mol}^{-1}$  (figure 11 (Mons *et al.* 2000a)). Similarly, one can measure the relative

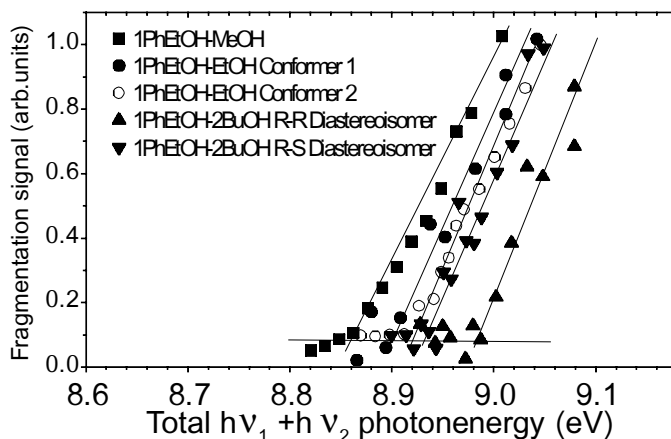


Figure 11. Fragmentation signal as a function of the two-photon energy from H-bonded complexes of the chiral alcohol (*R*)-1-phenyl-ethanol with a series of alkyl alcohols: methanol, ethanol (two different complexes) and (*R*)- and (*S*)-2-butanol, illustrating the higher binding energy of the *RR* diastereoisomer with 2-butanol compared with *RS* as well as the increase of the binding energy with the size of the alcohol alkyl group (Zehnacker *et al.* unpublished work).

stability of similar complexes with a series of alkyl alcohol molecules. Figure 11 shows the fragmentation signal of the complexes of (*R*)-1-phenyl-ethanol with various solvents: methanol, ethanol (two conformers) and 2-butanol (*R* and *S*). The increasing binding energy with the size of the alkyl group (about 1.0 kcal mol<sup>-1</sup> per CH<sub>2</sub> group) probably reflects the increase of dispersive interaction between the alcohol alkyl group and the aromatic ring of 1-phenyl-ethanol.

One should nevertheless point out that, when working with floppy molecules, specific complications do arise. Indeed, M–S complexes can be formed with different conformations of either M and/or S having different stabilities. Even the most simple chiral alcohol solvent, 2-butanol, already presents several conformations. A careful analysis (Mons *et al.* 2000a) showed that, if the solvent molecule is not in its most stable form in the complex, then the ion fragmentation threshold, which corresponds to the formation of the most stable conformation of the solvent molecule, will lead to an underestimate of the neutral dissociation energy. Owing to the spread in energy of the conformers of a molecule such as 2-butanol, errors as large as 1 kcal mol<sup>-1</sup> can occur in the  $D_0$  measurements if these effects are not taken into account. As a consequence, the conformation of both molecules *in the complex* has to be studied, for instance using IR spectroscopy.

Direct measurements of energetics on complexes larger than dimers are very scarce, for several reasons. First, the measurement of the evaporation energy from an M–S<sub>2</sub> trimer  $D_0^{(2)}$ , that can be defined as  $D_0^{(2)} = \Delta E(\text{M-S}_2 \rightarrow \text{M-S} + \text{S})$ , will be accessible only if the non-adiabatic photoionization threshold of the 1:1 complex is observed. Such an opportunity is offered in the case of phenol–water<sub>2</sub>. Since a very accurate adiabatic ionization energy of the phenol–water complex was reported by Müller-Dethlefs and coworkers (Dopfer *et al.* 1994), the evaporation energy of water from phenol–water<sub>2</sub> was recently determined (M. Mons *et al.* unpublished results). The value found ( $8.4 \pm 0.2$  kcal mol<sup>-1</sup>) corresponds to the energy necessary to break

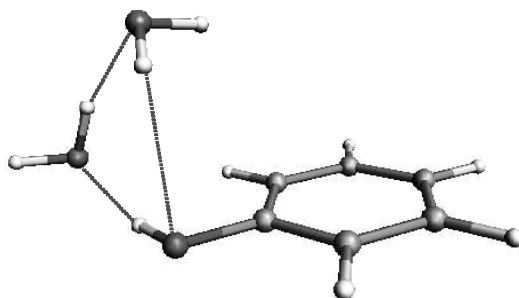


Figure 12. Phenol-(H<sub>2</sub>O)<sub>2</sub> complex: minimum energy conformation of the neutral complex (Brenner and Millié 1994).

two of the three H bonds of the cyclic structure of the complex, as determined by IR–UV spectroscopy (see figure 12 (Tanabe *et al.* 1993, Watanabe *et al.* 1996, Zwier 1996)). It appears to be substantially larger than the sum of the two broken bonds taken separately, i.e. *ca.* 6.8 kcal mol<sup>-1</sup> (estimated from the anisole–water and the water dimer bonds). The difference should be assigned to the cooperative effects in the cyclic structure. It should be noted that such measurements can be carried out only for those clusters that are small enough to keep the kinetic shift negligible (Spangenberg *et al.* 2000).

#### 4. Conclusion

The present review discusses in detail the possibility of measuring dissociation energies of gas-phase complexes from their DPI. The method relies on the ability to control, via the photon energy, the amount of vibrational energy deposited in the photoionized complex. Detecting the dissociation threshold in the ion enables one to measure the dissociation energy of the neutral species, using a simple energetic balance. In some cases, the energetics of the ionic species can also be determined.

Using this DPI technique, several types of hydrogen-bonded neutral complexes of aromatic molecules have been investigated:  $\sigma$  H bonds as well as  $\pi$  H bonds. Recently emphasis has been put not only on the most stable species, often the only form observed in the gas phase, but also on secondary solvation sites, opening up a wider approach to the potential energy surface of the complexes.

The present compilation of experimentally determined dissociation energies shows that experimentalists are beginning to provide a consistent set of energetic data that can be proposed as a valuable alternative to *ab initio* calculations and even as benchmarks to assess these calculations.

Several systems, as simple as Bz–HCl or Bz–HF, whose both *ab initio* calculations and experimental studies still have unresolved questions, deserve further investigation. However, with the recent development of gas-phase studies of biological molecules, one can predict a wealth of energetic results on complexes of biological interest in the near future. In particular, one can expect that doubly bridged species, in which for instance a water molecule is linked to a solute both as a donor and an acceptor (Matsuda *et al.* 1999, Florio *et al.* 2001), will be successfully studied. This would be interesting for their fundamental aspects since it would enable the quantification of the effects of cooperativity in H bond networks. Such



complexes are also of biological interest, since doubly bridged complexes are for instance relevant to the microscopic scale hydration of DNA bases.

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