Determination of binding energy in molecular clusters by ion imaging methods: A test on the phenol–water 1:1 cluster

F. Mazzoni, M. Pasquini, G. Pietraperzia, M. Becucci *

Chemistry Department 'Ugo Schiff' via della Lastruccia 3, and LENS via Nello Carrara 1, Polo Scientifico e Tecnologico dell'Università di Firenze, 50019 Sesto Fiorentino (FI), Italy

HIGHLIGHTS

- Tightly bound molecular clusters photodissociation.
- Velocity mapping imaging VMI for binding energy determination in molecular clusters.
- Good agreement between VMI and reference ZEKE/MATI data.

ARTICLE INFO

ABSTRACT

In this paper we present a test on the velocity mapping imaging approach for the experimental direct determination of the binding energy in clusters formed by strongly interacting polyatomic molecules. The method is applied to the phenol–water cluster, a system for which the binding energies were already determined in different experiments. The binding energy values that we obtained, 1975 cm^{-1} in the S_0 state, 2327 cm^{-1} in the S_1 state and 6586 cm^{-1} in the ionic D_0 state, are in very good agreement with the previous determinations. We report our results and we discuss advantages and limitations resulting from our experience.

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Introduction

Recently many experimental data have become available on molecular clusters [1–9]. The determination of the cluster structure is the key to access its properties and to evaluate the subtle balance of different terms in the intermolecular potential that is responsible for its stabilization. However the determination of the binding energy of the cluster provides an even more fundamental property of the system. Energies are the simplest quantities that are calculated in any kind of theoretical methods used for modeling of the intermolecular interaction.

The most precise structural determinations are obtained thanks to rotationally resolved spectroscopic data [6–8]. Even though the direct inversion from the moments of inertia to the structure cannot be done, a satisfactorily modeling of the system can be made with some minor assumptions. Alternatively, the frequency shift of selected vibrational bands can give an indication on the cluster geometry. In particular, this is the case of clusters formed by a

direct link of the two molecular moieties through a single interatomic coordinate: many hydrogen bonded clusters were studied thanks to hole-burning infrared-UV double resonance experiments [9].

The cluster binding energy is usually experimentally derived from microwave and infrared absorption spectroscopy, single and two photons ionization, dispersed fluorescence, and stimulated emission pumping [10].

Here we will focus on resonance enhanced 2 photon ionization (R2PI) experiments. In this case a pump and probe scheme is used where the pump laser is in resonance with a vibronic transition of the cluster and the probe laser is frequency tuned above the ionization threshold of the cluster. When the total excitation energy is above the dissociation threshold in the ionic state, the ion yields in the different mass channels change: increasing the available energy the ion yield at the mass of the fragments grows. In order to get further details on the dissociation dynamics and to determine more precisely the binding energy also ion imaging methods were used. The first publications based on velocity mapping (VMI) [11] ion imaging experiments were dealing mostly with studies on clusters formed by aromatic molecules with rare gas atoms [12,13].

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* Corresponding author.
  E-mail address: maurizio.becucci@unifi.it (M. Becucci).

In VMI arrangement, particles with the same velocity are focused in the same point of the detector. The detector is normally time-gated in order to select particles with a given mass/charge ratio. It is then possible to reveal the fragment ions formation from the selective excitation of a cluster and also to measure their recoil speed. The kinetic energy release (KER) from dissociation can be derived from the recoil speed. If the dissociation process is really statistical then it should be possible to observe production of fragments with the maximum kinetic energy (or, equivalently, with zero internal energy). With a single measurement, this experiment could provide an upper limit to the dissociation energy [14]. Otherwise, if measurements are repeated for different total excitation energies, it could lead to a clear picture of the fragmentation dynamics, potentially increasing the accuracy in the determination of the dissociation energy (both dissociation yield and maximum recoil energy are decreasing linearly to zero when excitation energy approaches the dissociation threshold). As in conventional R2PI experiments the fragment ion yield can be measured and used to determine the ionization threshold of the cluster.

This paper aims to validate the R2PI-ion imaging method for determination of the binding energy in tightly bonded molecular cluster and to discuss limits and possible sources of error in the experiment. The test was stimulated by the recent discussion on the S_0 binding energy determination of the anisole dimer due to the significant difference between calculated (1480 cm^{-1}) [15] and experimental (3926 cm^{-1}) [14] values. We report on a study of the phenol–water complex: a simple model cluster where a strong interaction exists, dominated by hydrogen bonding. The structure was clearly determined both by microwave and high resolution electronic spectroscopy [16,17]. The dissociation energy was already measured by the Neusser group in a mass analyzed threshold ionization (MATI) experiment carried out in a time-of-flight mass spectrometer [18]. The ionization threshold for the cluster was measured to be 64,024(10) cm^{-1} and fragments appeared only above 70,000 cm^{-1} excitation energy. In that spectral region the authors reported a very weak signal, much likely due to unfavourable Franck–Condon (FC) factors for the ionization from the S_1 vibrationless level. The onset for dissociation in the ionic ground state, D_0, was then set to 6520(50) cm^{-1}. That, in combination with the accurate spectroscopic data available for phenol and for the $S_1 \leftarrow S_0$ electronic transition of the phenol–water cluster, leads to the value of 1916(50) cm^{-1} for the binding energy in the neutral ground state. Different *ab initio* evaluations of the binding energy in the ground state are in reasonable agreement with the experimental values. Calculations based on the Möller-Plesset perturbation theory, with different basis sets, gave values between 1760 and 2416 cm^{-1} [19,20].

Experimental

The velocity mapping ion/electron imaging spectrometer was already described in previous papers [21,22]. We form the phenol–water cluster in a pulsed molecular beam by an adiabatic expansion of a gas mixture through a pulsed valve (500 µm nozzle) in a vacuum chamber. The mixture is prepared flowing helium at 300 kPa over a sample of phenol at room temperature: as phenol is highly hygroscopic the sample already contains enough water to observe the phenol–water cluster. The central part of the gas expansion is spatially filtered by a skimmer and enters into the interaction region where the background pressure is of the order of 10^{-6} mbar. To selectively excite the cluster and induce fragmentation we use a R2PI scheme. A first photon promotes ground state clusters to the S_1 electronically excited state (0_0^0 band of the $S_1 \leftarrow S_0$ electronic transition at 35,996 cm^{-1}) [23] and a second one brings the cluster above the ionization threshold. In order to observe dissociation, the frequency of the second photon is scanned and a large amount of internal excitation is provided to the clusters. We scan the frequency of the second photon between 33,300 and 34,900 cm^{-1}. Laser interaction takes place between the electrodes of an electrostatic lens that consists of repeller, extractor and ground. The velocity mapping condition is achieved by setting an appropriate voltage ratio between repeller and extractor, given the geometry of the experiment. We use a space separation of 15 mm between the electrodes with voltages set at 2000 and 1700 volts for repeller and extractor, respectively. The extractor voltage is optimized trying to get the maximum achievable resolution in the photoelectron spectrum of phenol. We show in Fig. 1 the 3D reconstruction of the 2D image of photoelectrons emitted from phenol. The radial distribution function is used to calculate the electrons kinetic energy (EKE) spectra. The "onion peeling" algorithm [24] is used for image elaboration and radial distribution determination. This photoelectron spectrum is used to calibrate the imaging detector. The calibration of the images can be immediately transferred to all the other particle distributions, provided the geometry of the experiment and the voltages (absolute values) are fixed. The images can be magnified increasing the time of flight of the charged particles, as to say, reducing the absolute value of the electrodes voltages. In case of experiments with ions the voltage reduction strongly affects the ions detection efficiency: in the present case a voltage at the repeller below 2000 volts is unpractical for the limited signal to noise ratio achieved. This factor represents a strong limitation in the present experiment as the momentum conservation law during dissociation allows only for a very low speed of the phenol fragments. In fact, the momentum of both particles released must be the same, and the speed ratio is then the reciprocal of the mass ratio. As phenol and water masses are 94 and 18 a.m.u., respectively, the speed ratio is

$$s_{water}/s_{phenol} \approx 5$$

In our excitation scheme we produce only phenol ions, therefore the resulting images have a very small radius.
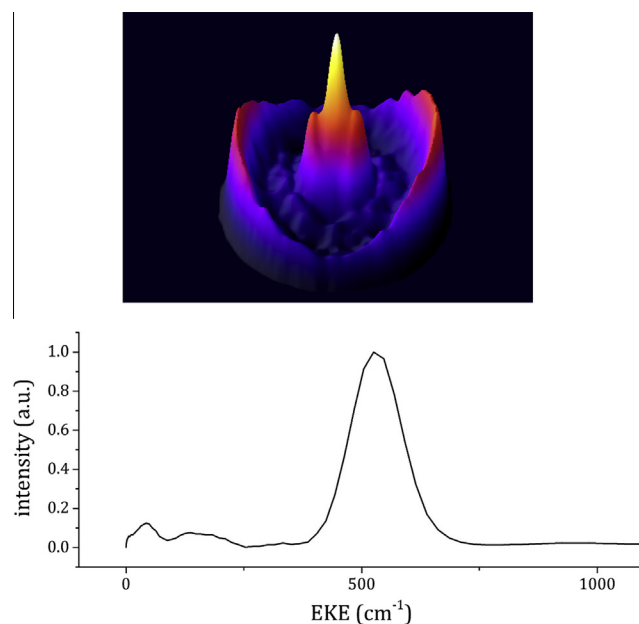

Fig. 1. Photoelectrons from R2PI experiment on phenol through the 0_0^0 band of the $S_1 \leftarrow S_0$ electronic transition. The total excitation energy is 69,151 cm^{-1}. 3D reconstruction of the photoelectron image on the 2D detector in use. False colors are used to represent the changes in intensity. The corresponding electron kinetic energy spectrum is also reported. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)