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Space – and – speed Slice Imaging of Molecular Photodissociation: Stereodirectionality and Chirality

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Abstract – Experimental techniques and interpretative tools of the physical chemistry of atmospheric and astrochemical elementary processes have been applied to specific aspects concerning the vast theme of molecular chirality. OrChiD is a project inspired by the open debate on the origin of homochirality, *i.e.* the phenomenon whereby classes of molecules have a single mirror shape (all aminoacids in proteins are left-handed while sugars in nucleic acids are right-handed) and from the high selectivity efficiency of the processes involving molecules of biological interest, in order to better understand mechanisms of chiral recognition. In this contribution, we report the role so far neglected of the effects of molecular orientation in kinetics of photochemical reactions.

Keywords: orientation; vector correlation; enantioselective mechanisms

Riassunto – Le tecniche sperimentali e gli strumenti interpretativi della chimica fisica dei processi elementari atmosferici e astrochimici sono stati applicati a temi specifici riguardanti il vasto tema della chiralità molecolare. OrChiD è un progetto che trae ispirazione dal dibattito sull'origine dell'omochiralità, cioè il fenomeno per cui classi di molecole presentano un'unica forma speculare (tutti gli amminoacidi presenti nelle proteine sono levogiri mentre gli zuccheri sono destrorigiri) e dall'alta efficienza con cui avviene la selettività di enantiomeri nei processi in cui sono coinvolte molecole di interesse biologico, al fine di comprendere meglio i meccanismi di riconoscimento chirale. In questo contributo illustriamo il ruolo finora trascurato degli effetti dell'orientazione sulla cinetica delle reazioni fotochimiche.

Parole chiave: orientazione; correlazione di vettori; meccanismi enantioselettivi

INTRODUCTION

The control of the translational, internal and orientational molecular states in physico-chemical processes in the gas phase allows us to obtain important information on the spatial characteristics of the molecules and on the aspects of the dynamics, which would otherwise be hidden by the chaotic movement of the molecules and constitute an important challenge for environmental, atmospheric, astrochemical modeling of pure and applied modern physical chemistry [1]. An important aspect is represented by chiral selection mechanisms [2, 3]. The aim of OrChiD is to characterize the enantioselective mechanisms, to verify the role of molecular orientation in the processes leading to chiral discrimination and to establish the stereodynamical nature of molecular chirality [4].

Molecular alignment and orientation are defined as non-statistical distributions of the rotational angular momentum with respect to a quantization axis [5, 6]. The alignment concerns the polarization of the direction of the angular momentum vector, while the orientation also considers its sense. We consider two techniques to control the molecular alignment and orientation: (i) the “natural alignment” makes use of a mechanical velocity selector, a device that permits to control the translational degrees of freedom of the molecules by selecting their speed in the beams and consequently the degree of natural alignment: this occurs in molecular flows, exploiting the “seeding” effect – the collisions induced by a light and fast gas, which transfers momentum to heavier and slower molecules, determining the phenomenon of their alignment [7, 8]; (ii) the hexapolar orientation technique, upon which we will focus in this contribution: it consists in coupling the aligning electric field of the hexapolar non-uniform electric field operated along the propagation axis of the molecular beam, to the orienting electric field of a second homogeneous field applied downstream [9, 10]. (For applications of hexapolar fields as rotational-state selectors see Ref. [11, 12] and as conformer selectors see Ref. [13]). The development of an experimental apparatus for the hexapolar electrostatic orientation to be coupled to an apparatus for molecular beams is therefore appropriate to verify photodirectionality and chirality effects in the dynamics of photodissociation processes [14], involving the interaction between possibly linearly polarized light and chiral molecules: the use of a non-chiral component, linearly polarized light rather than circularly polarized light, aims at verifying the role played by orientation of molecules in the mechanism of chiral discrimination. For a full understanding of this phenome-

non it is necessary to shed light on the way in which the three vectors that characterize the interacting system, the recoil velocity of the dissociating fragments \mathbf{v} , the permanent electric dipole moment $\boldsymbol{\mu}$ and the transition dipole moment \mathbf{d} , do correlate, giving chirality to the system itself. In Figure 1, we illustrate a scheme of arrangement of the vectors.

The paper is structured as follows: in Section 2, we report a description of the experimental apparatus; in Section 3, we give the results and discussion of the experiments; in Section 4, the conclusions close the paper.

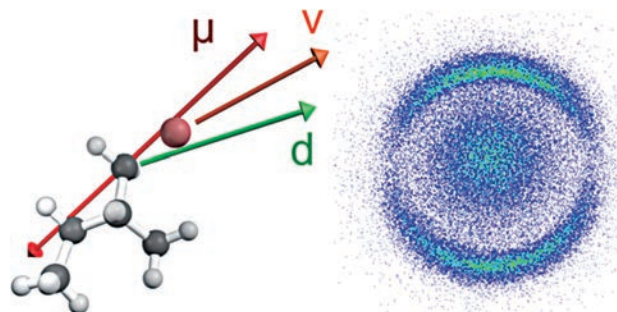


Fig. 1. The correlating vectors in 1-bromo-2-methylbutane (in the left) and the corresponding ion imaging (in the right): \mathbf{d} is the permanent electric dipole moment, $\boldsymbol{\mu}$ is the transition dipole moment, and \mathbf{v} is the velocity of the Br photofragment (the Br atom is represented as a red sphere; in black and white carbons and hydrogen, as conventional). (Adapted from Ref. [15]).

EXPERIMENTAL APPARATUS

In this project, the orientation of chiral molecules has been realized for the first time by electrostatic hexapolar technique, using weak electric fields [16]. These molecules have a complexity higher than the “asymmetric-top” molecules studied in previous experiments, containing a chain of four carbon atoms and the heavy atom bromine. The efficiency of the orientation was verified by combining time-of-flight measurements and slice ion-imaging techniques. For this purpose, two machines in our partner laboratories in Taipei and Osaka have been employed. It is important to stress that the hexapolar field allows us to select the rotational states (the single rotational state in the case of symmetric-top molecules or a certain distribution in the case of the highly dense states of asymmetric-top molecules), to select the distribution of conformers and to eliminate possible cluster contamination. Focusing also increases the beam intensity, making a wide variety of scattering and photodissociation experiments [13].

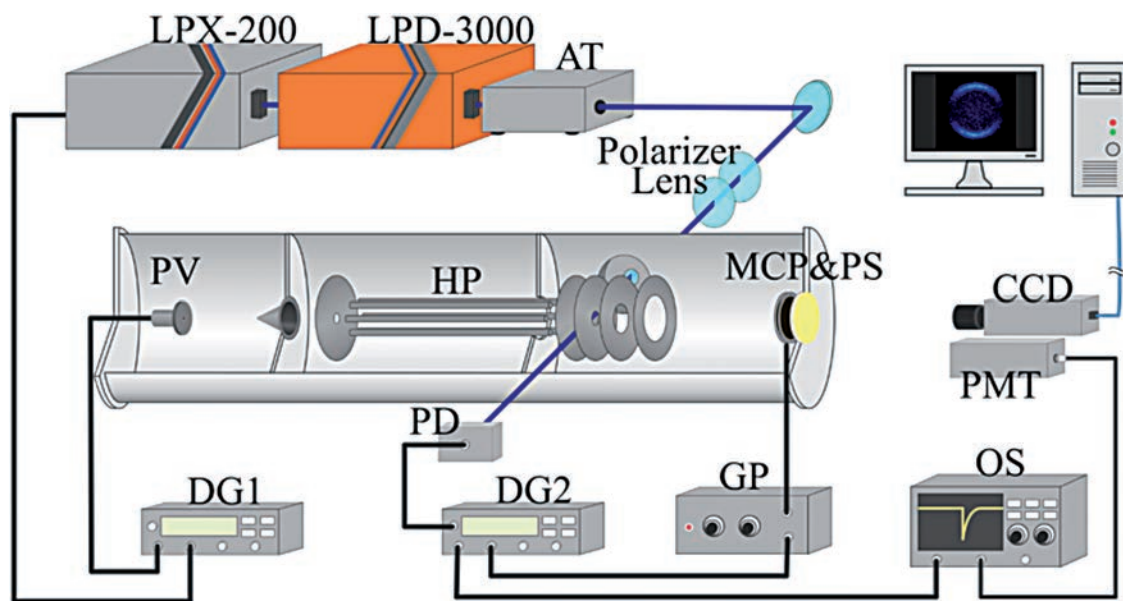


Fig. 2. The experimental set-up employed for photodissociation experimental at National Taiwan University in Taipei. (Adapted from Ref. 16). The scheme of the Osaka apparatus is exhibited in Ref. [17].

Figure 2 shows the Taipei experimental apparatus, essentially consisting of an excimer laser light which is doubled in frequency by a BBO crystal in the auto-tracker to obtain a photolysis / ionization source of photons of the desired wavelength. The sample to be photolyzed is emitted by a pulsed valve (PV) to form the molecular beam, which then passes into the hexapolar field (HP), where it is aligned, selected in rotational states and focused towards the region of intersection with the laser light. The laser and the pulsed valve are started by a pulse generator that synchronizes them. The fragment that is formed, for example bromine, is immediately ionized and mapped on a microchannel plate and phosphor screen (MCP & PS), and then recorded by a charge-coupled device camera (CCD). At the same time, the intensity and flight time are continuously monitored on an oscilloscope (OS) via a photomultiplier (PMT). The MCP is regulated by short low voltage pulses from the gate pulse generator (GP) to observe only the central slice portion of the ion cloud. Since the excimer laser has a slight instability in the production of the laser beam, usually 30 ns, the pulse is regulated by the photodiode (PD) via a pulse generator (DG2).

RESULTS AND DISCUSSION

Slice ion imaging detection applied to the photodissociation of 2-bromobutane at 234 nm, where Br (${}^2P_{3/2}$) is produced in the ground state, indicated as Br, and Br

(${}^2P_{1/2}$) in the first excited electronic state, here indicated as Br*: both the ${}^{79}\text{Br}$ and ${}^{81}\text{Br}$ isotopes were considered, allowing to shed light on the velocity distribution and on the angular distribution of the photofragments [16] and compared with a previous study [18, 19], that left an unsolved question regarding the attribution of a slow component of the photofragments of Br and Br*, under careful attention our experiments. A detailed analysis using the slice imaging technique has permitted the disentangling of the superposition of the ionic clouds of the two isotopes, ${}^{79}\text{Br}$ and ${}^{81}\text{Br}$.

It has also been shown how photodissociation experiments of oriented molecules can provide important information in processes involving highly dense rotational states and multiple transitions. Despite the high density of rotational states, population distributions controlled by the hexapole voltage are reflected in the angular distribution of atoms. The dependence on the dissociation wavelengths of the distribution of atoms was studied and the anisotropy parameter β was determined; due to the type of transition, perpendicular or parallel, which characterizes the photochemical processes. Since, in general, the analysis based on the combination of parallel and perpendicular components also applies to space-oriented molecule ion imaging experiments, this work serves a prototypical for planning studies where photodissociation takes place with the participation of transitions involving multiple and excited states. (In Figure 3, the energy level scheme involved in the dissociation of 2-bromobutane is represented).

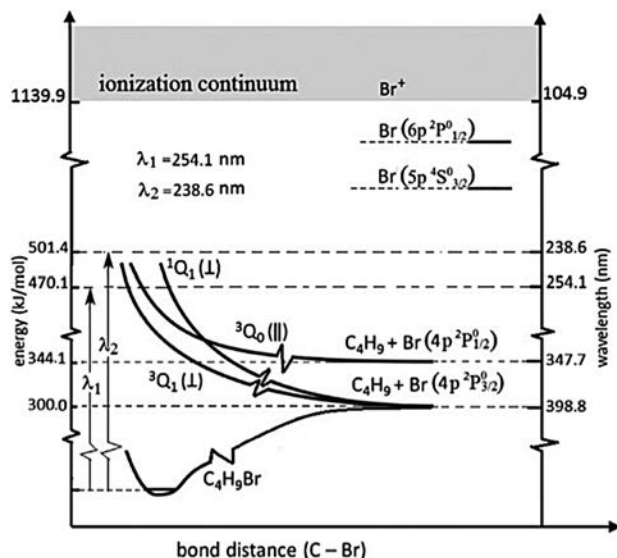


Fig. 3. The electronic states diagram of bromine atom. The energy of the radiation is given in kJ/mol and in nm, the C - Br distance is reported qualitatively. The laser wavelengths are indicated by $\lambda_1 = 254.1$ nm and $\lambda_2 = 238.6$ nm. (Adapted from Ref. [20]).

A further step forward was made with the study of the photodissociation dynamics of 1-bromo-2-methylbutane in a wavelength range between 232 and 240 nm, through “velocity map imaging” with an experimental apparatus with a single laser and with the action of two lasers [15]. The latter case, differently from previous works, consists in the use of a laser for photodissociation distinct from that for ionization: in this way it is possible to study a larger number of electronic transitions, allowing for the wavelengths of photolysis to cover band A, also improving the signal-to-noise ratio. The analysis of the imaging allows us to determine the parameters β of the various dissociative channels. Br^* is formed only after parallel transitions, while Br involves a combination of perpendicular and non-adiabatic transitions. The orientation of the original molecule, combined with quantum mechanical calculations and Monte Carlo simulations, allows us to evaluate the angles between the three vectors $d - \mu - v$. The angular anisotropy of the distribution of the Br fragment is smaller when the photodissociation wavelength is increased, suggesting an increase in the contribution from perpendicular transitions.

A further study of the photodissociation dynamics of 2-bromobutane through slice-ion imaging at wavelengths of 234 and 254 nm permitted to shed light on the correlation of the three vectors [21], extending the theory of the photodissociation dynamics of molecules to the case of oriented chiral molecules [22]. As for Br^*

this is mainly related to parallel transitions with a large anisotropy parameter and allows us to deduce that only one excited state is involved. The determination of the angles among the vectors, also in this case, permits to shed light on the structural properties of the molecule and on the spatial aspects of the dynamics. This result allows us, first of all, to establish what are the experimental requirements for obtaining chiral discrimination: the arrangement of the three vectors must be far from coplanarity, in order to favor the distinction of the angular distribution of the photofragments.

The ion lenses used in the “photofragment ion imaging” detection system produce an electric field of *ca.* 200 V / cm which acts as an ion extractor and allows molecular orientation. With the current set up it is not possible to change the intensity and direction of the orientating electric field. To overcome this drawback, a pulsed field has been added in the extraction phase to switch from “orientation mode” to “extraction mode”. Since ion extraction starts after the molecular beam crosses the photodissociation / ionization laser, it is possible to orient the molecules and extract ions separately on the time axis. As shown in Figure 4-a, where the flight time measurement of the Br (both ^{79}Br and ^{81}Br) formed following the dissociation of 2-bromobutane is reported, the slower peaks of both isotopes are increased by the addition pulsed voltage (red line) with respect to the signal with the fixed orientating field (black line). The pulsed field is applied in the first extraction stage in which the molecular beam and the dissociation laser are crossed, causing an inversion in the orientation of the molecule with respect to the propagation of the beam. This permits to detect Br with different times-of-flight, both for the mass number (79 or 81 depending on the isotope), but especially because of the orientation of the molecule.

Part (b) of Figure 4 shows the ion extraction phase. The pulse applied arises when the molecular beam reaches the repeller electrode (R) and lasts about 28 microseconds, ending just before the intersection with the dissociation laser. In this way, the pulsed field induces an orientation opposite to what one would normally have – this is the so-called “orientation mode”. If one removes the pulsed voltage, the electric field acts as an extractor, the so-called “extraction mode”. The response time of the pulsed field is very short, about 30 nanoseconds, and this allows one to avoid alterations of the peak along the propagation axis of the beam. This means that the pulsed field does not interfere with the extraction of the ions. To reverse the orientation (*i.e.* to arrange the molecule with the Br- end of the molecule is oriented to-

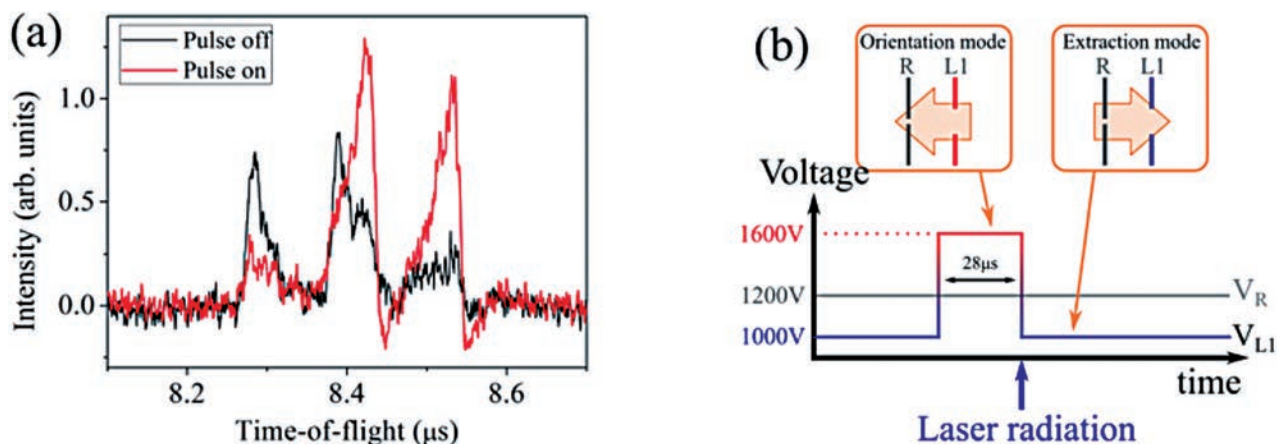


Fig. 4. a) The time-of-flight of the Br fragment from the oriented molecule (in red) and non-oriented molecule (in black). b) The electrostatic orientation arrangement. The electrostatic lens, R and L1, according to the voltage, work in the extraction mode and in the orientation mode. (Adapted from Ref. [16]).

wards the detector or in the opposite direction), a pulsed field of about 200 V/cm with opposite polarity with respect to the extraction field is applied. In this apparatus, the electric field can be increased up to 1.3 kV / cm for the “backward” orientation (see the red line of Figure 4-a) and 2 kV / cm for the “forward” orientation (see the black line of Figure 4-a). By decreasing the distance between the repeller electrode (R) and the first extraction lenses (L1), the orientating field can be further increased.

CONCLUSIONS

The investigations discussed in this issue permitted to shed light on photodissociation dynamics when chiral molecules are involved. The fundamental requisite to discriminate enantiomers of chiral molecules is their orientation, for which an advanced experimental setup has been built. Current limits for experiments of chiral selectivity have been also evidenced: for electrostatic hexapolar orientation it is necessary that the molecules have a permanent dipole moment that allows their interaction with electric fields. In experiments where laser beams are used the energy of the dissociating bond and that of ionization of the detected atom requires a wavelength of 200-260 nm, and this is the operational range for both the Osaka and Taipei machines. The choice of the candidate molecule relies on two main factors: the

detected photofragment must be originated from a well defined bond dissociation process and possible background contaminations must be avoided. For these reasons, the chosen molecules are derivatives of bromine and chlorine. For these reasons, our choice fell on bromine derivatives. A fundamental factor, related to the detection of chiral effects that permit to select different enantiomers, is related to the correlation of the vectors that define the system, which have to be out of plane to form a chiral arrangement. Many of the molecules examined show an almost coplanar arrangement, so that the distinction between the two enantiomers may not be detectable with current instruments.

The recently completed investigation of the photodissociation of haloethane, a simple chiral fluoro-chloro carbon, also containing bromine, has been shown to undergo simultaneous breakings of two bonds, C - Cl and C - Br bonds, with distinct orientations. This encourages the expectation of a candidate molecule for achieving on-the-fly separation of enantiomers [17].

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