

**Determination of energy-transfer distributions in ionizing
ion-molecule collisions
- Supplemental Material -**

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EXPERIMENTAL DETAILS

The experiments have been performed at ARIBE, the low-energy ions facility of GANIL (Caen, France) and at the GASPHASE beamline of the synchrotron radiation facility ELETTRA (Trieste, Italy). Both experiments are based on crossed-beam set-ups using coincidence time-of-flight mass spectrometry. The effusive beam of neutral thymidine molecule (2'-deoxy-thymidine) was produced by heating a powder (Sigma-Aldrich - 99% purity) in a molybdenum oven at 130°C. At this temperature, the thermal decomposition is avoided.

Ion collision experiment

In the ion collision experiment, the ion beam of O^{6+} at 48 keV is produced by an ECR source then pulsed in bunches of 500 ns and transported to the interaction region. The charged products resulting from the interaction of thymidine molecules with the ion beam are analyzed using a Wiley-McLaren linear time-of-flight mass spectrometer coupled with a Daly-type detector allowing a constant detection efficiency over a large mass range. The set-up allows also to measure fragment ion-fragment ion coincidences in order to study the fragmentation dynamics as a function of the initial charge state of the molecule.

Some peaks in the mass spectrum, shown in the Fig.1(b), are due to a contamination of the residual gas by previous experiments on PAH molecules (namely pyrene with mass 202 and anthracene with mass 178).

Photoionization experiment

The end-station used in the photoionization experiment consists of a Wiley-McLaren type time-of-flight mass spectrometer coupled to a 150 mm mean radius electron energy analyzer (VG 220i, with six electron multiplier detectors) in order to perform photoelectron spectroscopy (PES), photoion mass spectrometry (PIMS) and photoelectron-photoion coincidence measurements (PEPICO). In PES experiment the pass energy of the VG hemispherical analyzer was set at 5 eV corresponding to an energy resolution FWHM of 200 meV, while in the PEPICO it was 20 eV corresponding to FWHM of 800 meV.

FITTING METHOD

The overall mass spectra obtained by different methods look similar, the same peaks are observed differing only by their relative intensity. The range of binding energies E_b covered by the PEPICO experiments allowed to sample molecular orbitals up to $E_b = 15.74$ eV, therefore not all of the fragments observed in the ion spectrum (Fig.1b) are also observed in the photoionisation measurements (Fig.1h-k). In particular, more energetic processes induced by inner valence ionization and resulting in multiple H-losses, formation of smaller fragments ($m/q < 50$ amu) and fragments with a broad kinetic energy distribution have a reduced contribution or are completely absent in the PEPICO spectra. This corresponds to the tail towards larger excitation energy in Fig. 2. Thus further studies should include PEPICO spectra extending to higher excitation energies to fully represent the ion-induced mass spectrum.

In the present we have selected the 11 most intense peaks, present in both sets of data, to be implemented in the fitting procedure (Tab.SI).

The areas of the peaks of these eleven fragments in the ion (I_k) and in the thirteen PEPICO (P_{jk}) spectra have been evaluated by fitting Gaussian functions to their respective mass spectra. Then via a constrained linear least squares fitting procedure:

$$I_k = \sum_{j=1}^{13} A_j \cdot P_{jk} \quad (1)$$

where $k = 1 - 11$ is the index of the eleven charged species from $m/q = 31$ to 242 amu (see Tab.SI for the list) and $j = 1 - 13$ is the index of the thirteen measured PEPICO spectra, corresponding to increasing binding energies from 7.96 to 15.74 eV (see the inset label of Fig.S2 for the full list), we searched for the best values of the A_j factors that reproduce the intensity I_k of the ion fragments in the ion impact spectrum.

In the fitting procedure, we *i*) constrained $A_j \geq 0$ and *ii*) initialized the fit with a vector of thirteen random numbers. In order to sample a broad range of the multidimensional surface of the parameters, an arbitrary number of 10,000 repetitions of the fitting procedure, each one with a different set of initial parameters, has been performed. The result is reported in Fig.S1, together with the weight averaged χ^2 of all these solutions.

The frequency distribution of each one of the parameters A_j is displayed in Fig.S2 versus its value, demonstrating the good convergence of the fitting procedure. The half width of each

TABLE I. List of charged species implemented in the fitting procedure.

m/q	Assignment
31	HOCH ₂ ⁺
55	C ₃ H ₃ O ⁺
73	C ₃ H ₅ O ₂ ⁺
98	C ₃ H ₂ N ₂ O ₂ ⁺
	C ₄ H ₂ O ₃ ⁺
	C ₅ H ₆ O ₂ ⁺
99	C ₃ H ₃ N ₂ O ₂ ⁺
	C ₄ H ₃ O ₃ ⁺
	C ₅ H ₇ O ₂ ⁺
110	C ₅ H ₆ N ₂ O ⁺
116	(S-1) ⁺
117	S ⁺
126	(B+1) ⁺
127	(B+2) ⁺
242	dThy ⁺

distribution provides the uncertainty of the parameters, as reported in Fig.2 and Fig.S1

The comparison between the measured (I_k) and “reconstructed” ($I_k(\text{fit})$) distribution of intensity of the selected charged species in the ion spectrum is reported in Fig.S3. $I_k(\text{fit})$ is calculated according to eq.S1 and using the values of the A_j parameters corresponding to the black crosses in Fig.S1.

MOLECULAR ORBITALS

We show in Fig.S4 the highest occupied molecular orbitals (HOMOs) of thymidine computed with the Hartree-Fock method and with a basis set 6-311G(d,p). The energies in the figure corresponds to the ionization values computed with the outer-valance Green’s function (OVGF) method.

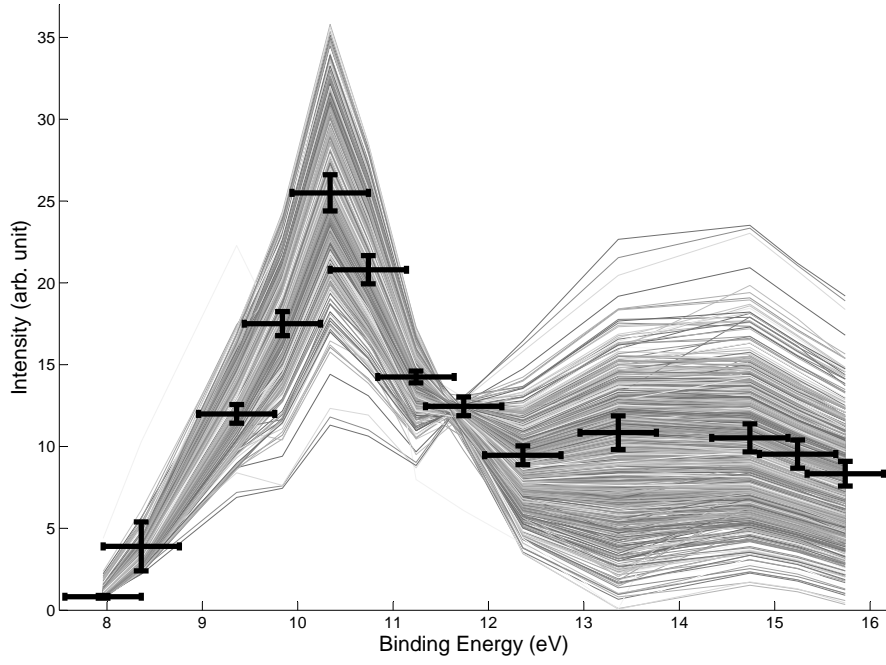


FIG. 1. The grey lines show the best values of the A_j parameters in the 10,000 repetitions of the fitting procedure reported versus binding energy. The black crosses are the weight averaged χ^2 of these solutions, reported with uncertainties in both binding energy (due to energy resolution in the PEPICO experiments) and averaged value (see text).

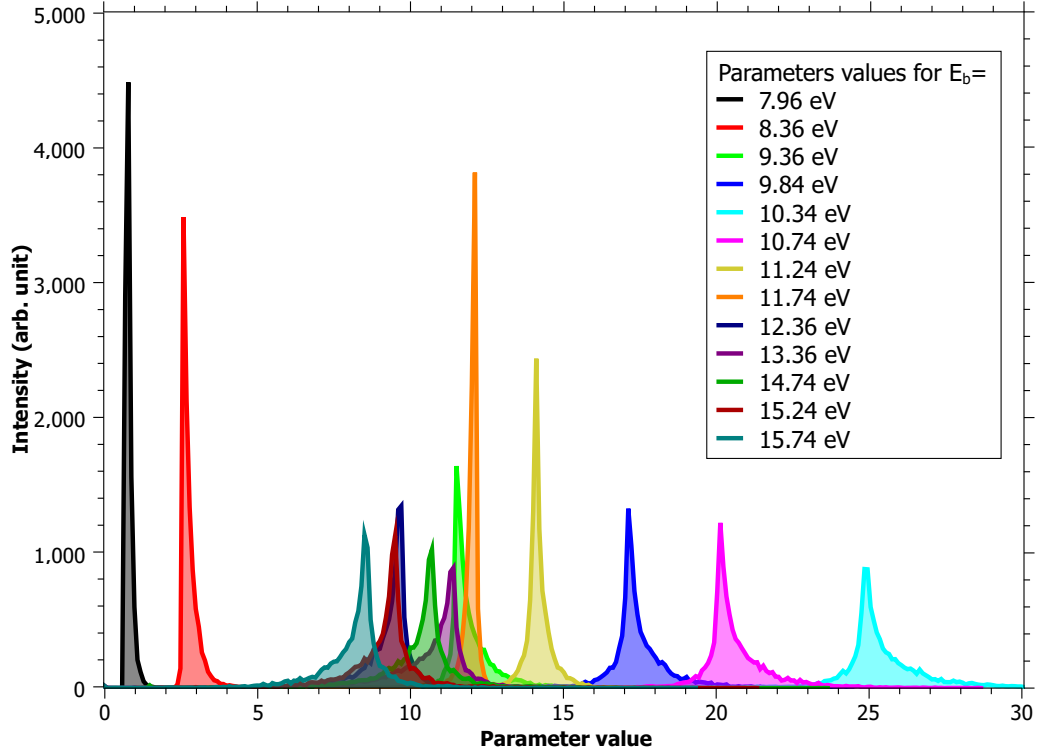


FIG. 2. The frequency distribution of the 13 A_j parameters reported versus their value. The correspondence between each parameter and the binding energy of the PEPICO spectra is given in the panel. The area of each one of these peaks is equal to 10,000 (number of fitting repetitions) while the half width provides an estimate of the uncertainty.

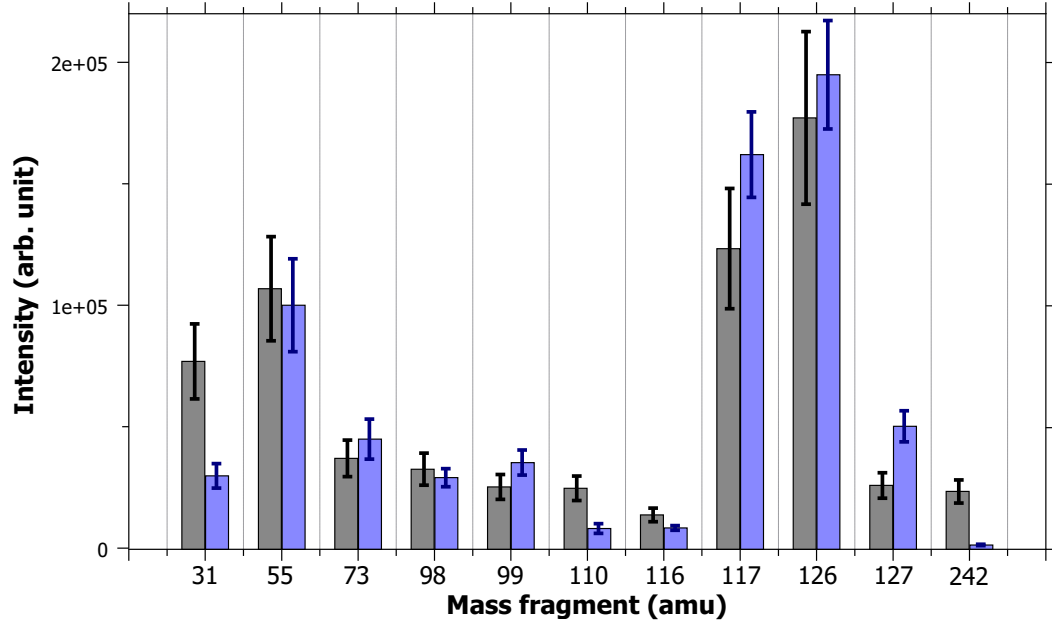


FIG. 3. Comparison between the measured intensity of the selected charged species in the ion spectrum (I_k , grey bars) and the one reconstructed by eq.1 ($I_k(\text{fit})$, blue bars), using the the best values of the A_j parameters reported in Fig.2 and Fig.S1

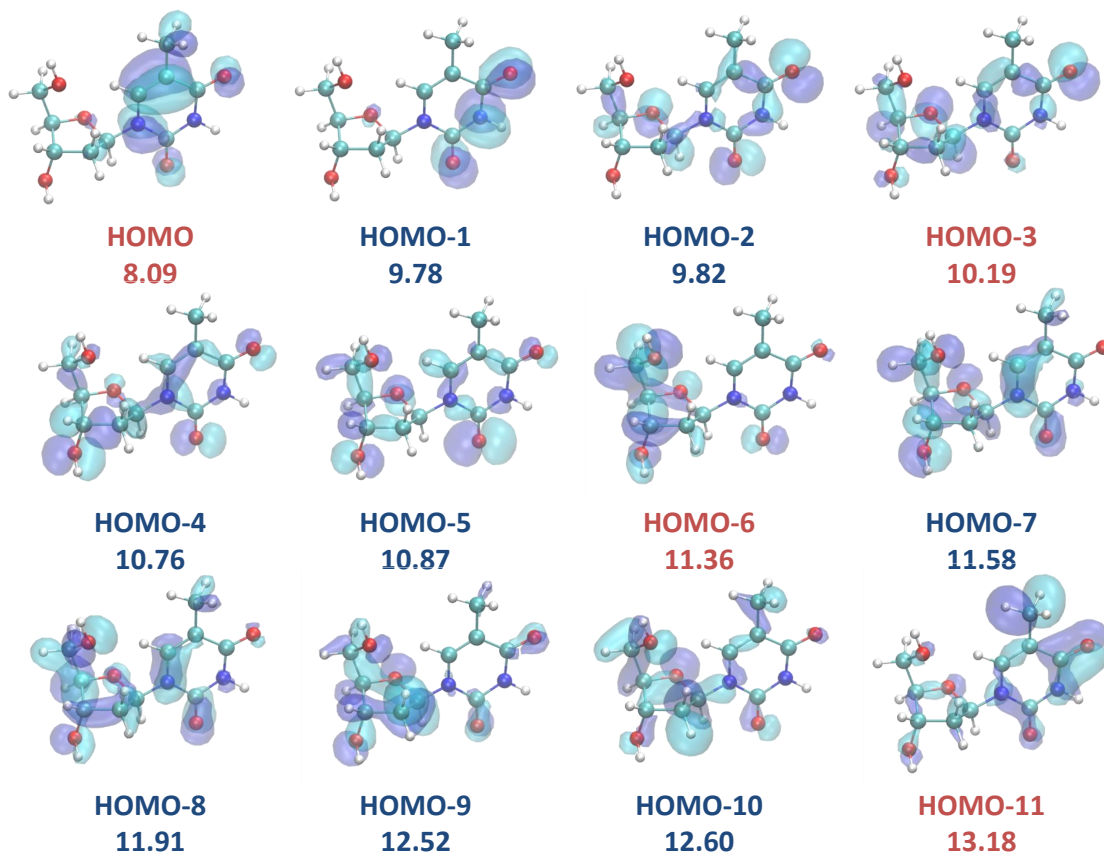


FIG. 4. Computed electron densities of the 12 highest occupied molecular orbitals (HOMOs). Ionization energies from each HOMO are given in eV. In red the orbitals discussed in the paper.