

PRELIMINARY STUDY ON KINETIC ENERGY DISTRIBUTIONS OF Ar^+ FRAGMENTS RESULTING FROM Ar_3^+ VISIBLE PHOTODISSOCIATION

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According to a strategy which involves DIM excitonic Hamiltonian, DIM-like transition dipole moments, realistic dynamical propagations with the HWD method (Hemiquantal dynamics with the Whole DIM basis), and the Wigner function to weight the initial conditions, a non-empirical theoretical study of the kinetic energy distribution of the Ar^+ photofragments is performed for three total energies. The results illustrate the dominant symmetric stretching motion and the importance of non-adiabatic effects in the Ar_3^+ dissociation dynamics.

The Ar_n^+ clusters have recently received increasing interest both from theoretical and experimental groups. Theoretical studies have been essentially concentrated on cluster conformations and stabilities investigated by DIM¹⁻³ and ab-initio^{3,4} methods. The main result was the localization of the charge on an Ar_3^+ core surrounded by nearly neutral atoms. Experimental investigations⁵⁻⁹ allowed the determination of the photoabsorption spectrum, the identification of the photofragments, and more recently the analysis of photofragment kinetic energy distributions (K.E.D.) by time-of-flight techniques. The assignment of Ar_3^+ as the chromophore in all clusters up to Ar_{13}^+ shows the importance of a good understanding of Ar_3^+ dynamics.

We have recently performed¹⁰ the first direct comparison between theoretical and experimental results in a study devoted to the visible photoabsorption spectrum of Ar_3^+ . Such calculations involved the determination of a reliable electronic Hamiltonian matrix, the computation of the transition dipole moments, and realistic (4-D, 6-electronically-coupled Potential Energy Surfaces (P.E.S.)) dynamical investigations. This study¹⁰ used in a consistent way a DIM excitonic electronic Hamiltonian, a DIM-like procedure for the transition dipole moment, and the HWD method (Hemiquantal dynamics with the Whole DIM basis) for the dynamics. These tools were involved in a non-empirical preliminary study which gave a clear physical interpretation of many experimental results: Ar_3^+ was found to be linear, the main absorption peak was assigned to a $\Sigma_u^+ \rightarrow \Sigma_g^+$ transition ($\mu \approx 5.3$ a.u.), and Ar^+ only was formed because the excited Ar_3^+ molecules rapidly dissociated along a symmetric stretching motion and remained on the excited electronic PES.

The same strategy is applied here to the determination of the kinetic energy distribution of Ar^+ photofragments in order to get a deeper understanding of Ar_3^+ dynamics which could be confirmed by comparison of our results with the T.O.F. experimental ones.

The recent experimental studies⁷⁻⁹ on the Ar_3^+ cluster reveal three peaks in the KED, corresponding to forwards and backward ejected fast Ar^+ atoms for the outer peaks and to Ar^+ atoms with nearly zero kinetic energy for the central one. This result fits nicely into our prediction that the system explodes along a symmetric stretching motion: the central peak comes from the slow central atoms which are not affected by the rapid separation of the two outer atoms. The latter Ar^+ atoms carry nearly all the excess energy and lead to the outer peaks of the T.O.F. spectra. It is thus easy to interpret the absence of kinetic energy for the central atom; however the presence of some charge on it is more surprising.

Our prediction that the visible spectrum corresponds to a $\Sigma_u^+ \rightarrow \Sigma_g^+$ transition was recently confirmed by an analysis of the anisotropy resulting from the use of polarized light.^{8,9} However for a Σ_g^+ electronic state of Ar_3^+ there is no charge on the central atom (as long as no *s* or *d* orbitals are involved) which is thus expected to appear as a neutral fragment. Due to bending and antisymmetric stretching deformations of the linear molecule a very low residual charge appears in the calculations

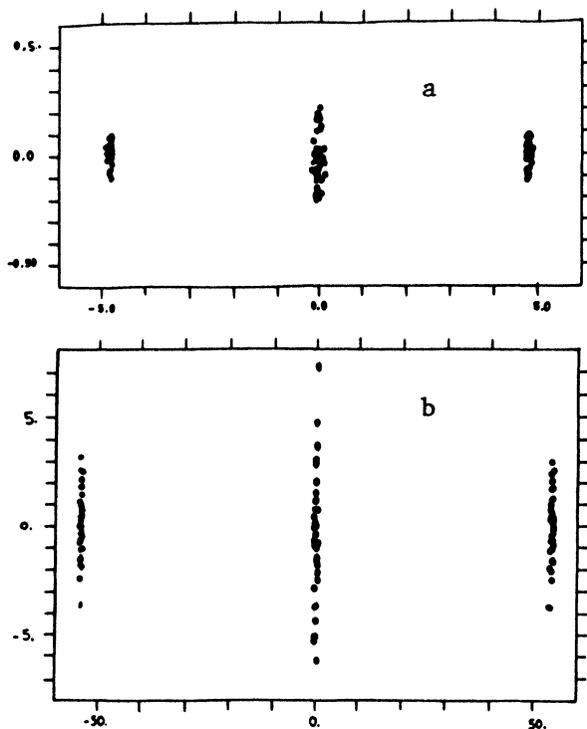


Figure 1 A typical set of geometries of the Ar_3^+ molecule. (a) initial geometries, (b) final geometries corresponding to HWD trajectories stopped for a hyperspherical radius larger than 100 a.u.

($\approx 10^{-2}$) but can absolutely not explain the central T.O.F. peak. The mechanism 2b of reference 8 ($\text{Ar}_3^+ + h\nu \rightarrow [\text{Ar} \dots \text{Ar}^+ \dots \text{Ar}] \rightarrow \text{Ar}^+ + 2\text{Ar}$) is not compatible with a Σ_g^+ electronic state and the interpretation based on it is invalid. On the other hand if classical trajectories are run on the second excited adiabatic PES, the system dissociates along a symmetric stretching motion but since the electronic wavefunction is not considered in such methods, at complete dissociation the charge should be

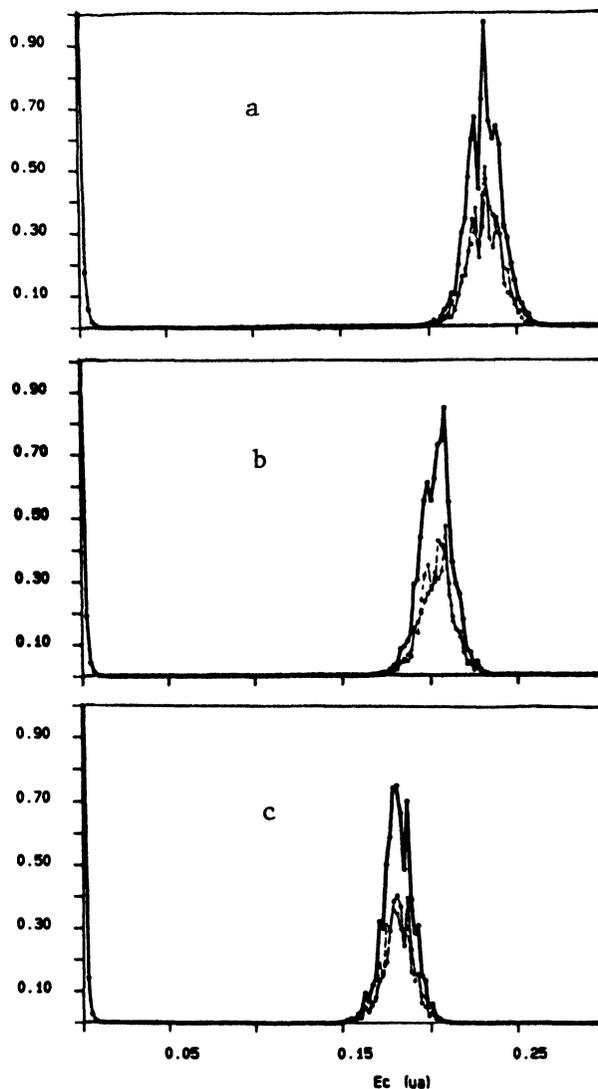


Figure 2 Kinetic energy distribution of the Ar^+ photo fragments for various total energies. (a) $E_{\text{tot}} = 0.6247$ a.u. (≈ 458 nm for the experimental excitation laser), (b) $E_{\text{tot}} = 0.6191$ a.u. (≈ 488 nm), (c) $E_{\text{tot}} = 0.6147$ a.u. (≈ 514 nm). Individual contributions from each of the Ar^+ atoms are also plotted.

equally shared between the three atoms, leading to an unrealistic result of three peaks with identical areas in the T.O.F.

The presence of some charge on the central slow atom results from the loss, during the dissociation, of the Σ_g^+ character of the initial electronic wavefunction. It can only be reproduced by methods involving explicitly the electronic wavefunction along with the motion of the atoms. According to our HWD investigations, the charge remains nearly zero during a large part of the dissociation and increases at large distances when all states tend towards full degeneracy. This is a typical non Born-Oppenheimer effect due to the non-adiabatic couplings and emphasizes the importance of a multistate dynamical treatment (such as the HWD method) in the context of cluster investigations.

To get quantitative results we generated a set of initial conditions weighted by the transition dipole moment and by the Wigner function and run HWD trajectories starting on the second excited state (the nearly Σ_g^+ one). Figure 1a shows a set of typical initial geometries and Figure 1b the corresponding geometries for the photofragments (the trajectories are stopped and plotted when the hyperspherical radius becomes larger than 100 a.u.). The scale of Figure 1b is increased by a factor 10 with respect to Figure 1a but remains similar. This similarity emphasizes that the dynamics mainly consists in a symmetrical expansion of the vibrational wavefunction. It shows clearly that central atoms move significantly (≈ 5 a.u.) only along a bending-like motion while the outer atoms span a distance ten times larger (≈ 50 a.u.) along a symmetrical stretching. Figure 2 corresponds to the KED of the Ar^+ photofragments at different wavelengths. There are two peaks, one at nearly zero kinetic energy resulting from the central atoms only, the other at an energy which depends directly on the laser excitation energy and results from the outer atoms (individual contributions are also plotted). Work is in progress to interpret the surprising structure appearing in all figures for both fast atoms.¹¹ The direction of the velocity here was not taken into account but from the individual contribution of each atom there is no doubt that we will get three peaks when performing a simulation of the experimental conditions.

In conclusion, a strategy which was very successful in the photoabsorption study provides a realistic calculation of the kinetic energy distribution of the Ar^+ photofragments. The results illustrate the importance of non-adiabatic effects in Ar_3^+ dissociation dynamics.

References

1. J. Hesslich and P. J. Kuntz, *Z. Physik D.* **2**, 251 (1986).
2. P. J. Kuntz and J. Valldorf, *Z. Physik D.* **8**, 195 (1988).
3. H. U. Böhmer and S. D. Peyerimhoff, *Z. Physik D.* **3**, 195 (1986).
4. H. U. Böhmer and S. D. Peyerimhoff, *Z. Physik D.* **11**, 239 (1989).
5. N. E. Levinger, D. Ray, M.L. Alexander and W.C. Lineberger, *J. Chem. Phys.* **89**, 5654 (1988).
6. Z. Y. Chen, C. R. Alertini, M. Hasegawa, R. Kuhn and A. W. Castelman Jr., *J. Chem. Phys.* **91**, 4019 (1989).
7. J. T. Snodgrass, C. M. Roehl and M. T. Bowers, *Chem. Phys. Lett.* **159**, 10 (1989).
8. T. Nagata, J. Hirokawa, T. Ikegami, T. Kondow and S. Iwata, *Chem. Phys. Lett.* **171**, 433 (1990).
9. T. Nagata, J. Hirokawa and T. Kondow, *Chem. Phys. Lett.* **176**, 526 (1991).
10. F. X. Gadéa and M. Amarouche, *Chem. Phys.* **140**, 385 (1990).
11. F. X. Gadéa and J. Durup, to be published.