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Expected strong angular dependence of multi-ionization cross sections of diatomic molecules

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In the framework of a simple (atomic) model, already developed by other authors to compare ionization cross sections for diatomic molecules oriented with internuclear axis parallel or perpendicular to an ion beam, we have calculated the dependence of multi-ionization cross sections upon any relative orientation of the internuclear axis and the impinging ion direction. The results of our calculations are shown to fairly reproduce experimental data recently published about doubly ionized CO molecules. They suggest caution and increased attention to these orientation effects in the determination of kinetic energy distributions of fragments, dissociation fractions, and branching ratios for highly ionized molecules. [S1050-2947(97)02703-0]

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The fragmentation of multi-ionized molecules is a subject of rapidly growing interest mainly because successive experimental advances have progressively allowed one to detect, identify, and analyze all the charged fragments simultaneously released by the dissociation of a single molecule. After a first step mainly devoted to the identification of those fragments, the state of the art presently allows one to perform a complete determination of their momentum distributions, which should permit the study of the dissociative processes themselves.

In the specific case of swift ion-molecule multi-ionizing collisions, a comparison between the time of interaction between the projectile and the molecule and the period of the molecule rotation leads to the conclusion that the molecule can objectively be considered as frozen during the collision. Therefore, one can expect that the ionization process—which is the main dissociative process concerned in high-velocity collisions—is sensitive to the orientation of the molecular internuclear axis with regard to the beam direction. In this way, Horvat *et al.* [1], studying the dissociation of CO molecules induced by 96-MeV Ar^{14+} ions, have recently published measurements of the total kinetic energy and angular distributions for the dissociation reaction $CO^{2+} \rightarrow C^{+} + O^{+}$. The angular distribution exhibits an anisotropic behavior, as many more events are occurring when the CO axis is perpendicular to the beam axis (the difference is found to be about 25% with regard to a relative parallel orientation).

A very simple and geometric model has been proposed by Wohrer and Watson [2] to study this orientation effect (one can refer to Wang *et al.* [3] for a study of the transfer process, with dissociative state formation of the residual target), in which the analysis is, however, limited to the study of two particular cases (the internuclear axis is parallel or perpendicular to the beam axis). We have extended this model to any orientation of the molecule with respect to the beam direction. This model is based upon two hypotheses. First, the molecule is considered as the association of two independent atoms and the resulting electron distribution is treated as the sum of the independent atomic ones. Second, the ionization cross sections are calculated in the independent electron approximation. This latter assumption and the use of the binomial law allow us to extend it to the case of fragments of high charges from one-electron ionization probabilities. This single-ionization probability is represented by $p(b) = p_0 \exp(-b/r_L)$ [4], where p_0 is the probability at zero impact parameter, r_L the radius of the removed electron shell (here the L shell is the outer one), and b the impact parameter of the collision, different for the two individual atoms of the molecule and dependent on the molecular orientation. The results of this model are not very sensitive to the r_L value, which can be easily calculated from the Slater formula [5]. In this treatment, the p_0 value is the only free parameter that has to be determined. We present in Fig. 1 the model calculations with two different p_0 values in comparison with experimental ones. These calculations have been made by averaging on any relative orientation and they allow us to determine the p_0 value, leading to a good agreement for the total cross sections. In both cases represented here, the agree-

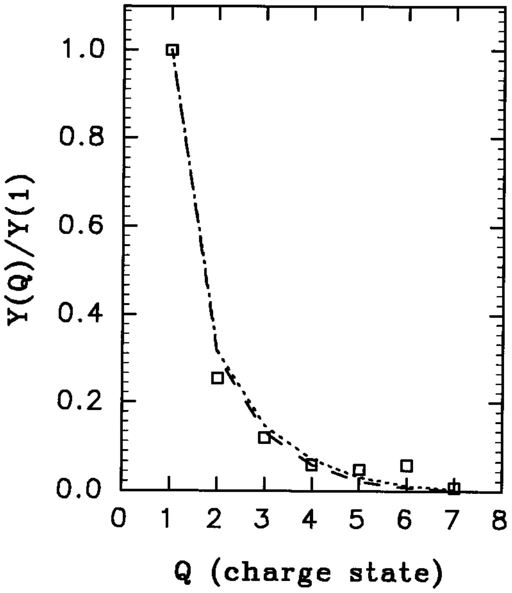

FIG. 1. Total multi-ionization cross sections vs the charge states Q. The results have been normalized to the $Q=1$ value. □, Experimental results from Wohrer *et al.* [7]; --- and ⋯ , this model calculation (see text) with $p_0=0.7$ and $p_0=0.8$, respectively.

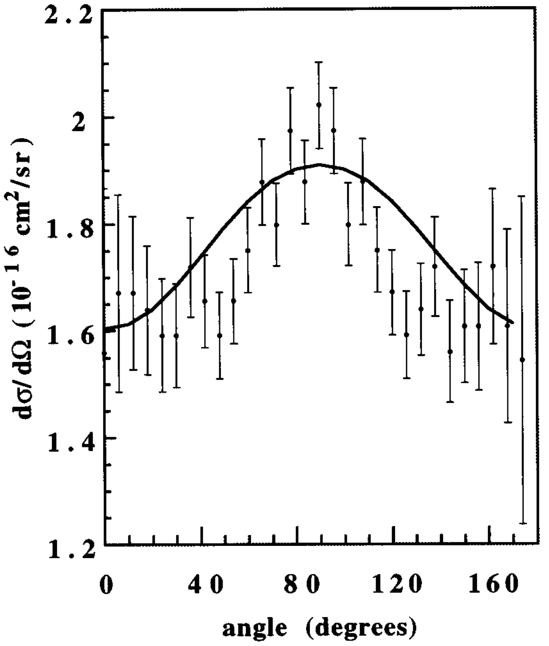

FIG. 2. Angular distribution for the double ionization of CO by 96-MeV Ar^{14+} projectiles. The experimental points are from Horvat *et al.* [1]. We have reported error bars taking into account statistical errors. The line is the present calculation.

ment is quite good. The general trend is well reproduced (except for the $Q=6$ value). Finally, the p_0 parameter is chosen equal to 0.8, for which the agreement seems to be better on the whole range of the charge states Q. We have used this value in the following calculations for each of the two atoms.

The presentation in Fig. 2 of the experimental data of [1]—the only ones published to our knowledge at the present time on the whole range of the angular values—in comparison with this model calculation exhibits good agreement. These calculations show that the multi-ionization is favorized by a perpendicular relative orientation. The shape and the amplitude of the experimental anisotropy of the dissociative double-ionization cross section are well reproduced by this calculation (Fig. 2).

We present in Fig. 3 the evolution of the multi-ionization cross sections—including the ten electrons of the C and O L shells—versus the relative angle between the internuclear axis and the beam direction, for the CO^{Q+} ($1 \leqslant Q \leqslant 10$) channels. In order to compare the evolution of the cross sections for each charge state, we have normalized these results to their 0° angle value (i.e., for a parallel orientation). For the low charge states (typically $Q \leqslant 4$), the cross section is found to be maximum for the perpendicular orientation with a quantitative effect that does not exceed 20%. The situation is quite different in the high charge state case ($Q \geqslant 5$). The parallel orientation becomes the preponderant one and the orientation effect is predicted to increase with the Q values and be important from $Q=6$. This change can reasonably be attributed to the fact that the multi-ionization process occurs for smaller impact parameters b than the single or double ionization processes. Therefore, a relative parallel orientation increases the probability for the projectile to pass at small impact parameters for both atoms and then to remove electrons from both in the same collision.

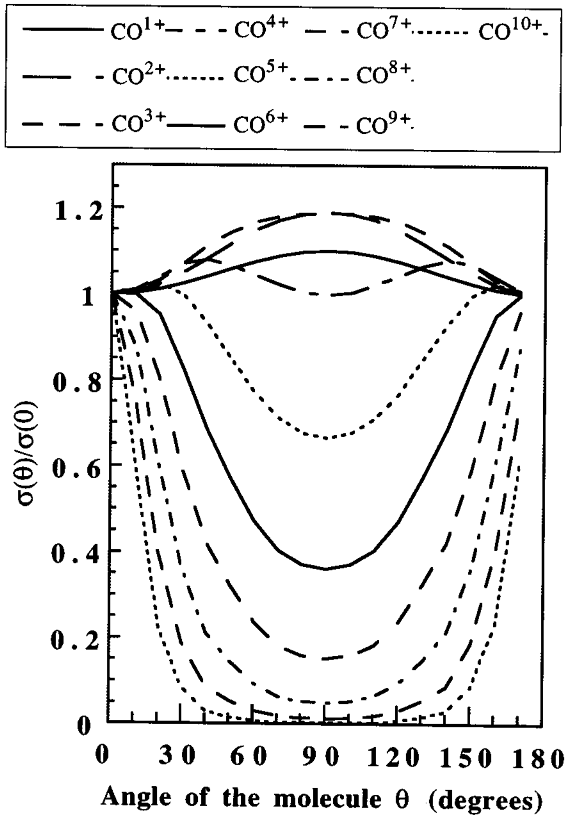

FIG. 3. Calculation of the angular distribution for the multi-ionization of CO (CO^{Q+} channels with $1 \leqslant Q \leqslant 10$). The curves have been normalized to their 0° value with a view to comparing the relative evolutions.

All the methods used up to now to extract the kinetic energy distributions (Sampoll *et al.* [6], Wohrer *et al.* [7], Ben Itzhak *et al.* [8]) of the emitted fragments have made the assumption that the angular discrimination can be neglected. Schäfer *et al.* [9], for example, have suggested a method to evaluate the kinetic energy distribution of single fragments based on a derivation of their time difference spectra (time difference between the two emitted fragments). This one—used, for example, by Ben Itzhak *et al.* [8]—is nevertheless limited to strong extraction fields (in order to collect all the emitted fragments) and we assume no angular preference between the molecule and the beam axis. Alternative methods such as the Scofield iteration one recently used by Sampoll *et al.* [6] or the photoion-photoion coincidence (PIPICO) used in photodissociation works (for example, Lablanquie *et al.* [10]), based on the deduction of the kinetic energy distribution from the time difference spectra via a transformation matrix, made equally this isotropic assumption. In fact, the results of the present model do not really refute the different analyses made previously, as only the low charged states have already been explored. The orientation effect is then expected not to play an important role compared to the accuracy of the currently extracted results. However, this brings the importance of the relative orientation between the beam and the molecule into light as soon as the attention is turned to fragments of higher charges. This anisotropic behavior will have, in the future, to be checked and if necessary taken into account in the transformation permitting one to deduce these kinetic energy distributions from the time-of-flight (TOF) spectra. These results, which are in good agreement with the first experimental data published for the double ionization case, suggest further investigation so that we can better understand the multi-ionization process.

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