Orientation Effects in Multiple Ionization of Molecules by Fast Ions

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The multiple ionization and dissociation of N_2 molecules by fast He^+ ions was studied by the coincident measurement of correlated fragment-ion momenta using a position- and time-sensitive multiparticle detector. The dependence of the cross section on the alignment of the molecular axis with respect to the beam axis was determined. The results show that for higher degrees of ionization the cross section has a pronounced minimum for molecules oriented perpendicular to the beam. The quantitative interpretation of the observed results is based on an extended version of the statistical energy deposition model.   [S0031-9007(97)03955-0]

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The multiple ionization and fragmentation of small molecules by energetic ion impact has attracted the attention of an ever increasing number of both experimentalists and theoreticians due to the fundamental importance of these processes in many areas of science and technology. The complexity of the ion-induced molecular fragmentation is mainly due to the variety of relevant mechanisms as well as its multielectron nature, which is strongly related to electron-electron correlation. In this situation it is advantageous to perform differential measurements which separate individual dissociation channels, and hence determine as much as possible the kinematical characteristics of the process.

Recent progress in the investigation of ion-molecule scattering is due to the use of the coincidence time-of-flight technique [1–3], which makes it possible to study different dissociation channels for highly ionized molecular ions. It has been shown that coincident measurements with a position- and time-sensitive multiparticle detector provide a complete three-dimensional image of the breakup process for each individual event [3]. In the simplest case of diatomic molecules this means that the dissociation of the highly ionized molecular ions can be studied for a definite orientation of the interatomic axis.

In the past decade, significant experimental and theoretical efforts have been devoted to studies of possible molecular orientation effects in fast ion-molecule collisions. Based on the ideas from the pioneering work by Tuan and Gerjuoy [4], the influence of the molecular axis alignment on the electron capture to the projectile ion and on the related processes of transfer ionization and transfer excitation was theoretically studied (see [5] and references therein). For these processes the alignment dependence has been interpreted as an interference effect in electron capture from the two centers of the molecule. When the diatomic molecule is oriented perpendicular to the beam there is a minimum phase difference between the amplitudes describing the scattering on the two centers, resulting in constructive interference. When the angle between the interatomic axis and the beam decreases, the phase

difference increases and the constructive interference diminishes. Therefore, if charge transfer contributes significantly to the ionization, one can expect predominant ionization of molecules oriented perpendicular to the beam. A strong alignment effect as predicted by theory was later confirmed experimentally in O^{8+} transfer ionization collisions with D_2 [6,7]. However, in this experiment as well as in proton collisions with H_2 [8,9] no alignment dependence was revealed in double ionization and ionization-excitation. This result was supported by calculations in the first Born approximation (cited in [10]) which showed that pure ionization of H_2 by proton impact shows relatively little (typically 20%) alignment dependence. For heavier molecules, a noticeable orientation effect was measured in the double ionization of CO molecules by 96 MeV Ar ions [11]; here also more ionization events were registered when the CO axis was perpendicular to the beam axis.

Very recently another orientation effect was considered theoretically [12,13] in direct multiple ionization of diatomic molecules by ion impact. Using a very simple two-atom picture and an independent electron model, a significant suppression of the multiple ionization cross section for the perpendicular orientation was predicted as compared to the parallel one, due to the purely geometrical effect of the nonisotropic electron density distribution. To the best of our knowledge, so far there has been only one attempt to measure the alignment dependence of multiple ionization in ion-molecule collisions [14]. The analysis of recoil N^{q+} ($q = 1$–5) ions, produced by a 19 MeV F^{9+} beam on an N_2 target, revealed that the production of the highest recoil charge states (4 and 5) preferred molecular alignment along the beam axis. This qualitative result corroborates the above theoretical prediction. However, a quantitative analysis of the data was not performed because of experimental complications.

In this somewhat ambiguous situation, we report here the first quantitative experimental results for angular distributions of highly charged molecular fragments in collisions of 100–300 keV He^+ ions with N_2 molecules as

well as a quantitative interpretation based on a statistical energy deposition model. Details of the applied experimental technique have already been published [15,16]; we will therefore give only a brief description of the experimental setup. Collimated beams of He^+ projectiles from a 350 kV ion accelerator interact with a N_2 gas target. The slow N^{q+} ions and electrons generated in the collision process are separated by a homogeneous electric field of 160 V/cm perpendicular to the projectile beam. Electrons are detected in a channeltron at one side of the interaction region; positive ions are accelerated towards the time- and position-sensitive multiparticle detector [15] at the other side. The detector system is triggered by the first electron registered by the channeltron. For each positive fragment the position (x_i, y_i) on the detector and the time of flight t_i relative to the start electron are recorded. From these data the initial velocity vectors of the fragment ions can be determined by the use of classical mechanics.

The present setup allows the separation and simultaneous measurement of all reaction channels which result in at least one electron and one or two positive fragments. The applied separation field is sufficiently large to establish a 4π-detection efficiency; i.e., all fragments are detected independent of their initial emission direction. Since the multiparticle detector is capable to resolve particles which arrive "at the same time" at different positions, the system is sensitive even to dissociations taking place in a plane parallel to the detector anode.

The dissociation of a multiply charged diatomic molecular ion results in fragment ions which emerge in opposite directions. In principle, the direction of the molecular axis at the instant of fragmentation could be derived from the velocity vector of one fragment alone if the position of the collision were accurately known. However, since the finite size of the gas target would limit the achievable angular resolution, we utilize the ability of our system to detect both fragment ions in coincidence. In this case a *kinematically complete* image of the molecular breakup can be derived for each individual event; thus, the precise knowledge of the start position is no longer needed and momentum conservation may be used for a consistency check. In the data analysis the direction of the molecular axis was derived from the measured positions and times for each electron-ion-ion coincidence.

Figure 1 shows the measured intensity as a function of the angle θ between the molecular axis and the projectile beam. We present the results for the projectile energy of 200 keV which are representative of similar results obtained for other energies in the interval 100–300 keV. The main contributions to the double ionization of N_2 consist of the symmetric Coulomb fragmentation $(N_2)^{2+} \rightarrow N^+ + N^+$ and the production of (meta-)stable N_2^{2+} ions. Only in the case of fragmentation is the orientation of the molecular axis experimentally accessible. The alignment dependence for the triply ionized $(N_2)^{3+}$
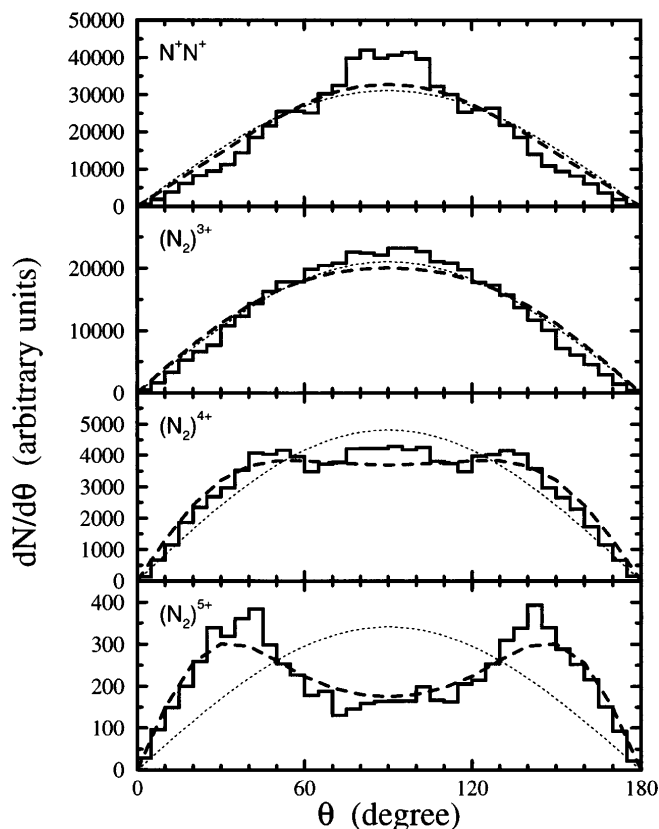

FIG. 1. Alignment dependence for the multiple ionization of N_2 molecules in collisions with 200 keV He^+ ions. Histograms show the experimental results, dashed curves are the theoretical results of the SED-LDA model, and dotted curves show the sine distribution. All of the curves are normalized to have the same area as the experimental histograms, and θ is the angle between the ion beam direction and the molecular axis.

was derived from the angular distributions for the reaction $(N_2)^{3+} \rightarrow N^{2+} + N^+$; in the case of $(N_2)^{4+}$ there are contributions from the channels $(N_2)^{4+} \rightarrow N^{2+} + N^{2+}$ ($\approx 85\%$) and $(N_2)^{4+} \rightarrow N^{3+} + N^+$ ($\approx 15\%$). Fivefold ionized N_2 mainly fragments into $N^{3+} + N^{2+}$. The experimental data are presented as histograms of ΔN versus θ with equally spaced angular bins. When the ionization cross section is independent of the orientation of the molecule, the number of dissociation events with angles between θ and $\theta + d\theta$ is proportional to $\sin\theta$. Our experimental data clearly indicate—at least for four- and fivefold ionization—significant deviations from the sine distribution, i.e., significant alignment effects. The alignment dependence for the highest degree of ionization shows a pronounced minimum at the perpendicular orientation in qualitative agreement with the prediction of the simple geometrical model by Wohrer and Watson [12].

In order to quantitatively interpret the experimental results, an extended version of the statistical energy deposition model (SED) was developed [17]. Based on the original ideas of Russek and Meli [18] and Cocke [19] the SED model implies that the probability of removing

n electrons from a system containing N correlated electrons is proportional to the phase-space volume available in a particular ionization state. This probability is directly related to the deposited energy and the ionization potentials of the various levels. It is assumed that the electrons are removed slowly in comparison with the collision time and rapidly in comparison with the nuclear motion in the molecule, a condition which is commonly expected to be fulfilled in the processes discussed. Therefore, multiple ionization is considered for a fixed-in-space molecule.

The deposited energy, i.e., the energy transferred to the electrons of the target, is equal (with negative sign) to the electronic energy loss of the projectile. We treat the energy deposition as a stochastic quantity fluctuating with respect to collision events. A distribution of deposited energies is characterized by its first (mean energy loss) and second (energy straggling) moments. We calculated the mean energy loss and the energy straggling using the well known local electron density approximation (LDA) of Lindhard and Scharff [20], which has been successfully used for a description of energy loss in ion-atom and ion-molecule collisions (see, for example, [21,22]). In this approximation every elementary volume of the target molecule is considered as a free electron gas with the density equal to the electronic density, $\rho(\mathbf{r})$. Then the mean energy loss of a particle of charge $Z_1 e$ and velocity v can be expressed as

$$-\frac{dE}{dx}(\mathbf{r}) = \frac{4\pi Z_1^2}{v^2}\,\rho(\mathbf{r})L(\rho(\mathbf{r}),v)\,, \qquad (1)$$

where $L(\rho(\mathbf{r}),v)$ is the usual stopping number. Convenient approximate expressions for calculating $L(\rho(\mathbf{r}),v)$ for a free electron gas have been suggested by Lindhard and Winther [23]. Using these expressions and Eq. (1) we calculated the mean transferred energy for a particle moving along a classical trajectory as a line integral of the right-hand side of Eq. (1) along the trajectory which we assumed to be rectilinear. Similarly, the energy straggling was calculated in the LDA for each trajectory using approximate expressions for the straggling in an electron gas derived by Bonderup and Hvelplund [24]. The electronic density of the N_2 molecule was calculated in the Hartree-Fock approximation using the MOLPRO computer program [25,26]. A full description of the developed version of the SED model with the energy deposition calculated in the LDA will be given elsewhere [17].

The multiple ionization cross sections calculated within the SED-LDA model for He^+ ion collisions with N_2 molecules at the ion energy of 200 keV are shown in Fig. 2 as a function of the alignment angle. The effective charge of the ion was chosen by fitting the total calculated energy loss to the experimental value. The resulting value $Z_1 = 1.65$ gives a reasonable estimate of the He^+ effective charge in this energy range. For convenience of comparison the calculated cross sections are divided by the cross section values at $0°$. The corresponding
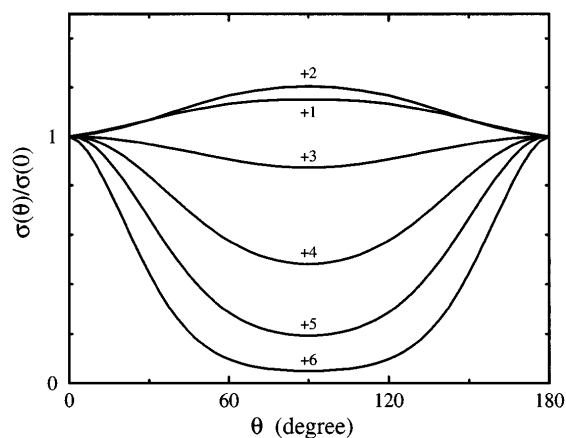

FIG. 2. The calculated cross sections for the multiple ionization of N_2 molecules in collisions with 200 keV He^+ ions as functions of the angle θ between the molecular axis and the beam direction. Curves are normalized at $\theta = 0°$.

absolute cross sections are presented in Table I where we give also the cross sections averaged over all orientation angles and multiple-to-single ionization cross section ratios. With this data we have calculated the total positive ion production cross section $\sigma_+ = 13.5 \times 10^{-16}$ cm^2 which compares favorably with the experimental cross section $\sim 12.6 \times 10^{-16}$ cm^2 [27]. The results presented in Fig. 2 agree qualitatively with those obtained from the simplified model [12,13]. At small degree of ionization the variation of the cross section with the alignment angle is weak with a slight increase at perpendicular orientation of the molecule relative to the beam direction. When several electrons are removed, the cross sections have a pronounced minimum at the perpendicular orientation which becomes deeper for higher degrees of ionization.

The origin of this strong orientation effect is the anisotropy of the electron density distribution [12] and the related anisotropy of the energy deposition along a trajectory. For a given ion trajectory the transferred energy and therefore the multiple ionization probability depends crucially on the molecular alignment. In order to remove several electrons large energy deposition is needed. When a diatomic molecule is aligned with the beam the probability of a large energy deposition is greater than for a perpendicular orientation because the projected

TABLE I. Calculated cross sections for the n-fold ionization of N_2 molecules with the molecular axis aligned with the He^+ beam [$\sigma_n(0)$] and averaged over all orientations (σ_n^{av}) in 10^{-16} cm^2, R is the ratio of the averaged cross sections $\sigma_n^{av}/\sigma_1^{av}$.

	σ_1	σ_2	σ_3	σ_4	σ_5
$\sigma_n(0)$	5.81	1.99	0.808	0.117	0.0139
σ_n^{av}	6.47	2.28	0.736	0.0733	0.005
R, %	100.	35.3	11.4	1.13	0.080

electron density sampled by the projectile is larger for trajectories close to the molecular axis. More pronounced alignment effects are expected with increasing degree of ionization since for those a larger energy transfer is required.

The calculated cross sections (multiplied by $\sin \theta$) are compared with the experimental data in Fig. 1. For higher degrees of ionization ($n = 3-5$) the theory describes the experimental alignment dependence well. It is interesting that for double ionization of N_2 the experimental distribution is peaked at 90° much more strongly than predicted by theory. One can speculate that this enhancement may be explained by the contribution of transfer ionization, which is not included explicitly in our model. In fact, the capture cross section for 200 keV He^+ is 2.6×10^{-16} cm^2 [27], i.e., about 20% of the total ionization cross section. Thus one can expect that the transfer ionization notably contributes to the double ionization. Our estimations show that the interference effect [5] can be very large at least for the dominant electron capture to the $2s, 2p$ levels of He. Therefore, the observed maximum at 90° in the angular distribution for double ionization (and possibly some excess cross section for triple and fourfold ionization) can probably be explained by the interference effect in the transfer ionization channel. More theoretical work is necessary to clarify this situation.

In summary, we have reported the first quantitative measurement of the strong effect of molecular alignment on the multiple ionization of diatomic molecules. The probability of ionization is larger when the molecule is oriented along the beam in comparison with the perpendicular orientation. The effect is stronger for higher degrees of ionization. Our experiment confirms earlier expectations [12] based on a simple "geometrical" consideration and the qualitative results of Ref. [14]. The extended energy deposition model gives a good description of the observed orientation dependence.

We note that competing ionization mechanisms give different orientation effects, therefore one can also expect that such measurements and a quantitative analysis of the angular distributions could shed more light on the dominant ionization mechanism.

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