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A coincidence detection algorithm for improving detection rates in coulomb explosion imaging

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ABSTRACT

A scheme for determining true coincidence events in Coulomb Explosion Imaging experiments is reported and compared with a simple design used in recently published work. The new scheme is able to identify any possible coincidence without the use of a priori knowledge of the fragmentation mechanism. Using experimental data from the triatomic molecule OCS, the advanced algorithm is shown to improve acquisition yield by a factor of between 2 and 6 depending on the amount of a priori knowledge included in the simple design search. Monte Carlo simulations for both systems suggest that detection yield can be improved by increasing the number of molecules in the laser focus from the standard ≤ 1 up to 3.5 and employing the advanced algorithm. Count rates for larger molecules would be preferentially improved with the rate for 6 atom molecules improved by a factor of up to five.

1. Introduction

The technique of Coulomb explosion imaging (CEI) is a developing field. The method involves removing many electrons from a molecule, which then explodes under Coulomb repulsion. By detecting all of these fragments in coincidence and measuring their complete momentum it is possible to measure the molecular structure. Methods of initiating such a multiple ionization process range from accelerating a molecular ion to several MeV and colliding it with a thin foil [1,2], colliding a highly charged atomic ion with a neutral molecule, or exposing a molecule to the intense electric field of a femtosecond laser pulse. The highly controllable nature of the laser pulse makes imaging of dynamics possible through pump-probe experiments [3]. Coulomb imaging apparatuses combine high resolution time-of-flight (TOF) mass spectrometry with position-sensitive detectors [4–7] to measure the momenta of all fragments from a Coulomb explosion in coincidence. Once a fragmentation channel has been determined and fragment momenta have been recorded, all the necessary information to reconstruct the molecular geometry is available [7–9]. In previous work we have shown [10] how geometry reconstruction can be optimized using a simplex algorithm to match measured asymptotic momenta with the results of a classical trajectory calculation, here we concentrate on optimization of coincidence detection in order to enable us to tackle more complex systems and to improve the statistical accuracy of our geometry reconstruction.

The methodology of coincidence analysis is largely undocumented in this field. However, it is crucial to the successful reconstruction of molecular geometry and it is essential for the development of Coulomb imaging as a mature and reliable technique that the efficiency of coincidence detection be maximized. In this paper, we will concentrate on the method of laser induced multiple ionization, which has the big advantage that it can promptly initiate the ionization of a controllable number of molecules per laser shot by adjusting the target molecule density. This allows the detection efficiency restrictions (50% per ion) to be countered. However, it has the drawback that false coincidences may result, that is, ions from more than one molecule may be detected and interpreted incorrectly. The simplest method to ensure that only genuine coincidences are recorded is by having no more than one molecule in the laser focus per laser shot. By way of Poisson statistics, this criterion can be met within 5% by having on average $\lambda = 0.35$ molecules in the laser focus per shot. This value has been stretched but maintained below 1 [4,11]. Such count rates have been adopted by the majority of experimenters allowing them to keep the ratio of true to false coincidences overwhelmingly high. The cost for this guarantee is in the final detection rate of true coincidences. In the case of triatomic molecules and 50% ion detection efficiency, the successful coincidence detection rate is approximately 0.05 molecules per laser shot. In order to investigate polyatomic molecules using detectors with such efficiencies, overall coincidence detection efficiency decreases exponentially [12] and so high count rates become a necessity.

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An important aspect of measuring genuine coincidences is the identification of ionic species through the TOF technique. This has been accomplished by considering molecules with fragments having a combination of distinguishable charge to mass ratios and distinct orientation dependent TOF such as CS2, and CO2, and by avoiding ions with degenerate charge to mass ratios (OCS: O^{n+}& S^{2n+}) or several identical atoms. In these latter cases, sophisticated analysis techniques are required for coincidence analysis even when low count rates are employed.

In this paper we develop an algorithm to handle high count rates and charge to mass ratio degeneracy and compare it with a simple and intuitive algorithm used in previous studies [7,8]. The effectiveness of these algorithms is simulated for diatomic, triatomic, and polyatomic (6 atom) molecules.

2. General analysis technique

The CEI apparatus is, at its most fundamental, a time of flight mass spectrometer combined with a position sensitive detector (PSD). A molecule in the laser focus, stripped of many electrons, can fragment due to Coulombic repulsion into atomic ions with charge to mass ratio (q/m). By measuring the location of impact on the PSD (x, y) and the time of impact (t), the asymptotic momentum vectors can be calculated using the equations:

$$P_x = \frac{m(x-x_0)}{t}$$

$$P_y = \frac{m(y-y_0)}{t}$$

$$P_z = \frac{qE}{2}\left(\frac{t_0^2-t^2}{t}\right)$$

where x_0, y_0, and t_0 are the zero momentum positions and time of flight. E is the electric field (constant for the experiment), while q and m are the charge and mass of the impact ion. For TOF systems with a constant accelerating field, ions can be identified by their mass to charge ratio using the relationship:

$$t_0 = \sqrt{\frac{2d}{E}\left(\frac{m}{q}\right)}$$

where d is the ion flight length defined by the laser focus location. Unlike traditional mass spectroscopy, ions arrive earlier and later (forwards and backwards) with respect to t_0 due to the explosion momentum imparted in the TOF direction. As a result, wide TOF windows are needed to identify detection events as specific ions. Frequently – and especially in the case of degenerate charge to mass ratio species – these windows overlap, causing uncertainty in identifying events with the TOF technique.

Though it is not possible to say with certainty that a single event has been correctly identified as a specific ion, it is possible to test a collection of events detected in a single laser shot by considering the net momentum. Assuming that the parent ion is at rest to begin with, the momentum sum of the fragment ions should be zero (to within a thermal limit). In most systems, the initial momentum is anisotropically Maxwellian, so the complete condition is the union of the coordinate sum:

$$\cap_j^{x,y,z}\left\{\left|\sum_i^{Ions}\vec{P_j^i}\right| < PT_j\right\} \quad (1)$$

where PT_j is the momentum threshold for the j'th axis. In experiment, PT_j is limited by either the target molecule thermal distribution (~3e-23 kg m/s for room temperature systems down to 1e-27 kg m/s for those employing super-sonic molecular beams) or detector resolution (~1e-23 kg m/s). If a subset of the detected events passes this test, it can be considered that the ions were correctly identified as a coincidence event-in other words, they were produced from the same molecule.

3. Coincidence technique

For situations where the number of detected events rarely exceeds the number of expected ions from fragmentation (i.e. $\lambda=0.5$), a simple algorithm can be used. CO2, SO2, and CS2 have all been studied using an approximation of the algorithm that follows [4,7,8] so, we will consider only the triatomic case. In CEI, data is extracted and collected in terms of fragmentation channels. For example, OCS- > $O^{2+}+C^{+}+S^{4+}$ is characterized as the (2,1,4) channel. Consequently, we first define such a channel:

$MQTW = \{\{mass, charge, low\ TOF\ limit, high\ TOF\ limit\}_i\}\ \ 1 \le i \le$ Number of Ions

The first two items in this set define the i'th ion via mass and charge (MQ) while the last two items define the TOF window (TW) used to identify a detected event as the i'th ion. In addition to these standard TOFMS definitions is the set $\{\{x_0, y_0, t_0\}_i\}$ used to calculate the i'th ion momentum.

The following algorithm assumes that three or more events were detected. Each event is identified through the index EventNum and processing begins with the event, which happens last (i.e. the arrival of the final ion at the detector). IonNum is an index that begins at 1 and tracks, which ion is being identified (and runs up to 3 in the case of the triatomic molecule). An event is successfully identified as an ion if the event TOF falls within the ion TOF window defined in *MQTW*.

1. If event EventNum is in the TOF range of ion number IonNum, increase IonNum. Increase EventNum.
2. Loop step 2 until IonNum > 3 or EventNum reaches the number of events collected in the laser shot. In the former case, go to step 3, in the latter case, the apparatus failed to detect ions in coincidence.
3. With the list of successful ion identities, perform momentum discrimination by applying condition (1). If this is successful, then the 3 events have been correctly identified as specific ions coming from the molecule under investigation.

The simplicity of this approach is clear and it can be very successful provided the ions arrive in the order that the TOF windows are defined. Systems such as CO2 and SO2 are therefore ideal targets.

In response to the limitations of the simple treatment described above, we have developed an algorithm, which can identify combinations of ions whose identity cannot be simply determined by their TOF. With the previous definition of terms, a list of potential ion identities is generated by iteratively processing each event against each *MQTW* entry. The collection of these lists forms a potential ion matrix (PIM). As an example, consider the data in the first two columns of Table 1. Testing this data against the ion TOF windows defined for O^{+}, C^{+}, and S^{+}, the PIM (last three columns of Table 1) is generated. After the creation of the PIM, the following actions are performed.

1. First element in the PIM is selected and a potential match is searched for in the following event entries.
2. If an ion in the PIM is found that is different from the first, a third ion is searched for from the beginning of the following row. Once a third unique ion is found, the collection of PIM indices—and thus ion identities—is recorded.
3. Search for the third ion continues with the following row. Once the search for the third ion has exhausted the PIM, the algorithm returns to search for a second suitable ion.