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Construction of a shuttered time-of-flight mass spectrometer for selective ion detection

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By placing a pulsed, high-voltage steering plate between the ion source and detector in a time-of-flight mass spectrometer, the signal-to-noise ratio of the mass of interest is improved by more than an order of magnitude. This improvement arises from (1) suppression of ions of other masses formed at the same time as the ion of interest and (2) suppression of ions formed at different times and different locations whose arrival time at the detector is nearly coincident with the mass of interest. The advantages of this simple device are demonstrated in the detection of molecular hydrogen in the presence of other species.

INTRODUCTION

A generic time-of-flight mass spectrometer (TOF/MS) consists of an ion source and an ion detector separated by a comparatively long drift region[1] (Fig. 1). The ion source emits a burst of ions at time $t = 0$. These ions are accelerated through a potential drop, pass through a drift region, and impinge upon a detector at times t_1, t_2, etc. Because ions of different masses arrive at the detector at different times, the measurement of the arrival times, t_i, allows the masses of the ions to be determined.

In most mass spectrometric studies, the entire mass spectrum is of interest and must be recorded.[2] However, there are special applications where the detection of only a single mass is desired. Examples are dynamical studies,[3] in which a reaction product must be detected, and spectroscopic studies of one-photon or multiphoton ionization.[4] For these applications, in which high mass resolution is usually not required, TOF/MS has been extensively used because of its high sensitivity, ease of implementation, and flexibility in the selection of the mass of interest.

The TOF/MS technique relies heavily upon the existence of a well-defined time of formation of the ions at a specific location. In practice, this may be accomplished by pulsed electron-impact ionization[1] or pulsed photoionization.[4] In the case of neutral particle TOF with continuous ionization,[5] chopping or pulsing of the neutral particle beam(s) serves to define $t = 0$. A problem arises if there are processes that create detectable charged species at times other than $t = 0$ and at various locations. In this case, other masses will be coincident at the detector with the desired mass, causing spurious events as well as substantially degrading the signal to noise.

In this article, we describe the construction of a device for suppressing interference from ions of other masses. This is accomplished by placing a steering plate approximately midway between the ion source and detector in the TOF/MS (see Fig. 1). Suitably pulsing the voltage on this plate causes it to act as an ion shutter, which is open to transmit only the ions of interest. The shuttered TOF/MS substantially decreases the ion current impinging on the detector. This has several favorable consequences, including the reduction of ringing in the detection electronics and the enhancement of detector life and performance.

We illustrate the application of this device in the detection of the HD reaction product formed in the hydrogen-atom bimolecular exchange reaction: $H + D_2 \rightarrow HD + D$.[6] The H atoms are generated in the presence of D_2 by laser photolysis of HI at 266 nm in a 1:3.5 HI:D_2 mixture. The HD product is detected in a quantum-state-specific manner. A second ($\sim$200 nm) laser source effects (2 + 1) resonance-enhanced multiphoton ionization (REMPI) via the HD E, $F\,^1\Sigma_g^+$ ($v = 0$) state, and the resultant HD^+ ions are detected by TOF/MS. This problem is particularly challenging because the small HD^+ ion signal must be quantitatively measured in the presence of a large background of other ions, such as HI^+, I^+, and I_2^+.

I. EXPERIMENT

Figure 2 shows a schematic of the experimental apparatus. Gas is introduced into the vacuum chamber via a quartz nozzle or may be bled through a leak valve. By focusing the output of a pulsed laser, ions are formed between two charged plates separated by 5.5 cm: the repeller (typically $\sim +700$ V) and the extractor (~ -350 V). The latter has a slit (8 mm wide, 4 mm high) through which the ions are accelerated into a second, differentially pumped chamber (pressure differential between the two chambers is $\sim$100). Note that the repeller is a grid, increasing the pumping speed

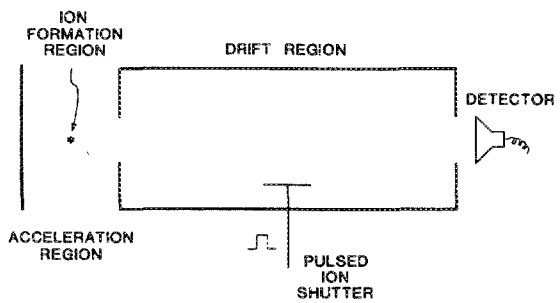

FIG. 1. Schematic diagram of a generic time-of-flight mass spectrometer showing a pulsed shutter for selective ion detection.

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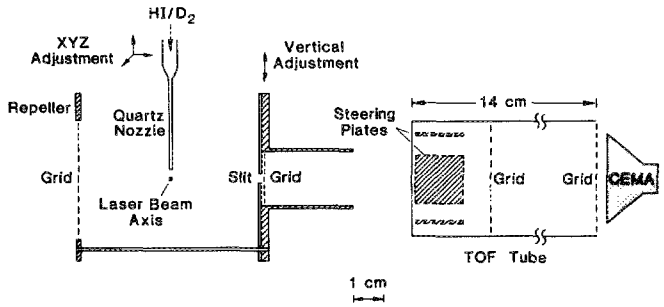

FIG. 2. Diagram of the shuttered TOF/MS used to study the $H + D_2$ reaction.

between the plates. The ions pass by two pairs of orthogonal steering plates before entering the TOF tube (~ -400 V, length $= 14$ cm). The drift region is defined by two grids charged to the same voltage as the TOF tube. After passing the second grid, the ions are detected by a CEMA (multichannel plate) detector. All components are electrically insulated from each other and from ground. Stray fields are minimized by floating all surfaces in proximity to the ion path.

There are two problems with the standard apparatus described above. First, there are many more ions formed at other masses than at the desired mass. This can be seen in Fig. 3(a), which shows an oscilloscope trace from a single laser shot. The desired mass peak ($m/e = 3$ for HD^+) is a factor of 10 smaller than the high mass peak ($m/e = 127$, 128 for I^+, HI^+). Although this does not directly interfere with the HD^+ signal, it results in a large ion current impinging on the CEMA, increasing the noise and decreasing the lifetime of the detector.[7] Second, there is a large, unresolved background caused by ions of various masses being nearly coincident at the detector with the mass of interest [Fig. 4(a)]. These secondary ions are formed at different times and locations than the ion of interest and arise from scattered light (from either laser) and/or ionization caused by secondary electron impact.

In the apparatus shown in Fig. 2, the voltage on one of the steering plates is pulsed. It is usually at ground, preventing ions from reaching the CEMA, and is pulsed to approximately -400 V (exact voltage chosen to optimize the signal

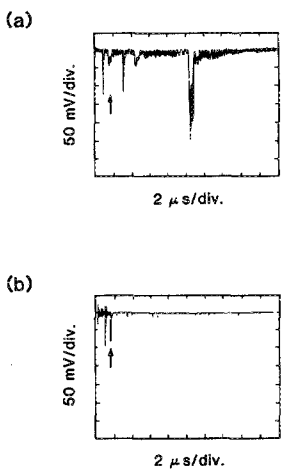

FIG. 3. Oscilloscope trace of a single laser shot, showing the time-of-flight spectrum: (a) steering plate is not pulsed, and (b) steering plate is pulsed. An arrow marks the position of the $m/e = 3$ peak of interest. Note the large current of high-mass ions in (a).

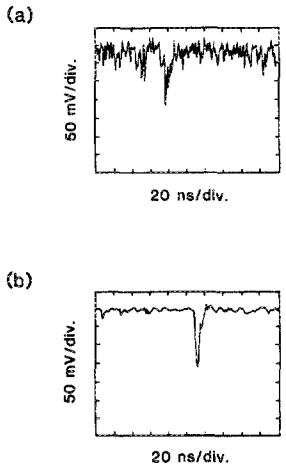

FIG. 4. Oscilloscope trace of a single laser shot, showing the region around $m/e = 3$ (expanded view of the region of interest in Fig. 3): (a) steering plate is not pulsed, and (b) steering plate is pulsed. Note the large background of secondary ions in (a).

at the desired mass) for ~ 500 ns (rise time ~ 100 ns). This pulse is delayed with respect to the laser pulse in order to transmit only those ions with the desired mass. The delay time and pulse width are set by a pulse generator (Hewlett–Packard model 8015A) triggered by the optical pulse from the ionization laser.

II. RESULTS

With the above apparatus, the large ion current at masses other than that desired is effectively eliminated and the signal at the desired mass is nearly free from contamination by secondary ions. These effects are shown in Figs. 3(b) and 4(b), respectively.

The ions formed by the laser pulse separate by mass before reaching the pulsed plate (ion shutter). Only those ions which reach the plate while it is charged to ~ -400 V can continue toward the detector. These ions further separate by mass before detection. Thus, the pulsed steering plate acts as a shutter in front of the TOF detector; it is usually closed, but opens briefly to allow the passage of the ions of interest. Other interfering masses may also pass by the plate if they arrive at the shutter when it is open, but these will separate from the desired ions in the TOF tube before striking the detector.

It is necessary to position the ion shutter approximately midway in the ion trajectory to eliminate both the high-mass signal and the secondary ion background. Placement of the shutter too close to the ion source would not allow sufficient mass separation before the shutter to exclude the high-mass ions. Placement of the shutter close to the detector would allow the passage of the secondary ions. With the shutter located approximately midway in the ion trajectory, TOF ion separation occurs twice (before and after the shutter). Thus, the apparatus is effectively a tandem TOF/MS, with the two TOF regions separated by the shutter. A similar device, called a "mass gate," has been used by Brucat *et al.*[8] for selection from a pulsed beam of cluster ions of an ion of a particular mass for subsequent study.

It is possible to use a pulsed grid as a shutter rather than a plate.[9,10] A plate is preferable because the ion trajectories are very sensitive to the voltage on the plate, and so there is little "leakage" when the shutter is closed. In addition, all

grids have some transmission losses. It is experimentally convenient, but not essential, to use a steering plate as the shutter rather than having separate steering and shutter plates.

Ogorzalek Loo *et al.*[11] have constructed a pulsed extraction TOF/MS, i.e., a TOF/MS in which the acceleration plates are pulsed to define $t = 0$. This represents the extreme of placing the shutter at the ion source. This arrangement does not prevent the high-mass ions from impinging on the detector. The pulsed extraction TOF/MS is most useful when the entire mass spectrum is to be recorded. The shuttered TOF/MS is preferable when selective mass detection is desired. Thus, in an experiment in which undesired masses are not present or are not to be excluded, the shuttered TOF/MS may not offer an advantage.

It is seen in Fig. 4 that the arrival time of the HD^+ peak is shifted when the pulsed steering plate is on. This arises from acceleration of the ions by the plate as it is being pulsed. It causes no problems when the desired region of the TOF spectrum is known. Since the peak shape is also distorted, this apparatus is not useful for applications where the peak shape is of interest; in such applications, a pulsed grid orthogonal to the ion trajectory would be a preferable shutter.[10]

The use of a shuttered TOF/MS is general and may offer advantages in any study where a limited range of ion masses is to be selectively detected.

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