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Mean kinetic energy of molecular fragment ions from time-of-flight and momentum analysis

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Abstract

The mean kinetic energy of molecular ion fragments derived from the variance of their time-of-flight distribution is found to be in agreement with the values based on their momentum spectra, measured simultaneously. Electron impact on CO_2 is taken as a test case. The problem of estimation of mean kinetic energy of ions of a given species arising from differing precursor states is also addressed. This analysis verifies the proposition, that the variance of the time-of-flight distribution is a robust estimate of the mean kinetic energy, as opposed to the commonly used estimate based on the square of the FWHM, which is an under-estimate. We also suggest a reliable method for determining the baseline and the extent of the time-of-flight peaks.

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Keywords: Molecular fragmentation; Fragment ion kinetic energy; Time-of-flight variance; Time-of-flight spectrometry; Momentum spectrometry

1. Introduction

Time-of-flight spectrometry has an enormous following, because of its simplicity. Perhaps surprisingly, it appears to be exploited by workers with contradictory purposes. A TOF spectrometer, when utilised primarily for mass-analysis, is designed to reduce the spread in time of ions of a given m/q as they reach the detector. The time spread is largely governed by two factors, namely the kinetic energy distribution of the ions when they are born, and the spatial extent of the source of these ions. An ideal TOF spectrometer would nullify the effects of both, and give a delta-function lineshape in the TOF spectrum. The Wiley–McLaren design [1] and the Reflectron [2] are attempts to this end. However, achieving high mass resolution is not always the sole purpose of a TOF instrument. As a matter of fact, by avoiding the complications of design which are necessary for reducing the effect of the kinetic energy spread on mass resolution, it is possible to use a TOF instrument for measuring the kinetic energy of ions. This idea has found following in the atomic collisions community, and in conjunction with recent particle imaging and multiple coincidence techniques, has gained ground as a powerful tool for studying a host of atomic collision systems as well as molecular fragmentation [3–7]. In this paper we consider the issue of obtaining a representative value for the kinetic energy of molecular fragment ions from the TOF lineshape, in the light of the proposition of von Busch [8], that the variance of the TOF lineshape is a robust estimate of the mean kinetic energy.

2. Preliminaries

The single stage Wiley–McLaren design is suited for the purpose of ion kinetic energy determination [1]. This design comprises an ion extraction field E_s over length s, followed by a field-free drift of length $2s$. The TOF of an ion of mass m and charge q is approximately given as

$$t = 2\left(\frac{2s}{E_s}\right)^{1/2}\left(\frac{m}{q}\right)^{1/2} - \frac{p_z}{qE_s}, \tag{1}$$

where p_z is the momentum of the ion along the spectrometer axis at the instant of formation. The approximation is correct

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to first order in p_z for $p_z^2/2m \ll qsE_s$. In general, p_z has a distribution $f(p_z)$, leading to a TOF distribution $l(t)$. Unless stated otherwise, we shall assume throughout the paper, that the momentum distribution $f(p)$ is isotropic.

Wiley and McLaren show, that for two equal energy ions, one of which is ejected towards and the other away from the detector, the difference in their flight times Δt is related to their kinetic energy U_0 via:

$$U_0 = \frac{(qE_s\Delta t)^2}{8m}. \tag{2}$$

This expression is correct as long as p_z is the only momentum component. However, the simplicity of this expression has led to its widespread use even in the case where other components of momentum are significant. When used thus, Δt in the above expression is substituted by the FWHM of the line, and the resultant is multiplied by a factor of 3 to take into account the equipartition of energy. Thus, the following representative value for the kinetic energy is obtained:

$$\langle K^{\Delta}\rangle \simeq \frac{3(qE_s)^2(\Delta t)^2}{8m}. \tag{3}$$

Clearly, the value thus obtained is not the mean value of the KE distribution. It has been shown by von Busch [8] that this quantity is invariably an under-estimate of mean KE, especially in the ubiquitous circumstance of Gaussian fitting to $l(t)$ for determining Δt. The main reason for the under-estimate is insufficient weighing of the tails of the peak. In contrast, the mean KE is exactly related to σ_t^2, the variance of the TOF distribution, through

$$\langle K^{\sigma}\rangle = \frac{3(qE_s)^2\sigma_t^2}{2m}. \tag{4}$$

In practice, both estimates are to be corrected for instrumental broadening and velocity discrimination in the spectrometer. If the TOF peak of a singly-ionised atomic target or undissociated molecular ion is measured under identical conditions, its width can be taken, for most purposes, to be the instrumental width, and can be used for correcting Eqs. (3) or (4). The variance based estimate is robust, because the tails of the distribution are properly accounted for. It is to be noted, that in the case of a Gaussian lineshape, FWHM is equal to $2(2\ln 2)^{1/2}\sigma_t$, so that mean KE obtained from Eqs. (3) and (4) disagree by a factor $2\ln 2$.

There are very few experiments which do not suffer from velocity discrimination in either transport or detection of ions. It is very often the case, that the acceptance is very high if the velocities are more or less along the extraction axis, but is poor for emission perpendicular to the extraction axis. This results in a time-of-flight line shape with truncated tails (or multiple peaks due to more than one energy group), biasing the estimates of kinetic energy of ionic fragments. This is of special concern in dissociative ionisation, which may be associated with high kinetic energy release. An additional complication arises in these experiments, in that $f(p)$ is not a unimodal distribution. Multiple dissociation pathways are open, resulting in overlapping distributions, arising from combinations of various excited precursor states. In such cases, estimation of mean KE purely on the basis of TOF widths can lead to grossly erroneous results. More importantly, experiments based on TOF measurements rarely have access to energy dispersion measurements, and vice-versa, leaving open the question of reliability of TOF based estimates.

The use of large area position-sensitive detectors for ion detection has improved the situation. An immediate consequence is that the increased area improves acceptance of transverse emitted ions. The far-reaching consequence is that position-sensitivity enables determination of the transverse momentum components. The exact expression for the mean kinetic energy, which is useful when all momentum components are measured, is:

$$\langle K^{\mathbf{p}}\rangle = \frac{\overline{p_x^2} + \overline{p_y^2} + \overline{p_z^2}}{2m}. \tag{5}$$

Devices employing the Wiley–McLaren TOF design in combination with position-resolved ion detection are in use as momentum spectrometers [9,10]. If it is ascertained, that the transverse acceptance is sufficient for the collision system under investigation, a momentum spectrometer offers an opportunity to verify or refute the validity of the variance based estimate. Considering that the use of TOF spectrometers is ubiquitous, and robust estimates of mean energies are often more convenient than the entire distribution, this aspect assumes significance. In the following sections we describe the kinetic energy analysis of fragment ions using a momentum spectrometer, and compare the estimates of the kinetic energy based upon the FWHM of the TOF peak, the variance of the TOF peak, and the squares of the momentum components (Eqs. (3)–(5) respectively). All raw estimates are subject to correction for instrumental broadening, based on the width of the peak of an atomic ion or an undissociated molecular ion.

3. Details of the momentum spectra

Details of the momentum spectrometer can be found in [11], only a brief description is presented here. The spectrometer is a combination of a single field time-of-flight spectrometer and a position resolving detector. The ion acceleration region is 11 cm long followed by drift region of 22 cm, in conformity with the Wiley–McLaren condition $d = 2s$ [1]. The ion detector is a channelplate of 76 mm open diameter, with a position-encoding delay-line anode [12]. Position resolution of 250 μm and timing resolution of 500 ps are specified. Ion detection involves simultaneous derivation of a fast timing signal of the particle hit and its position on the detector. Besides the ions, ejected electrons are also detected, after acceleration over 3 cm in the opposite direction. The electron detector is a 40 mm diameter channelplate. The TOF start is obtained from the ion-hit, while the stop is obtained by a delayed coincidence with the ejected electron. The ejected electron is solely used for the purpose of TOF coincidence, its kinematics are not analysed. Ion TOF (t) and position (x, y) information is stored event-by-event as (t, x, y) triplets, and the event list can be sorted at will. The spectrum of any one of the three variables can be obtained by simply ignoring the other two in the event triplet. More importantly, conditions can be set on one variable, and events satisfying those conditions

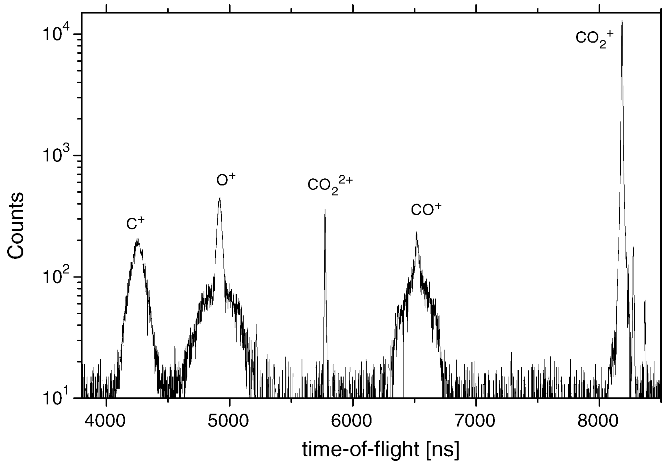

Fig. 1. A TOF spectrum of ions arising from 1300 eV electron impact on CO_2, after subtraction of background. The two sharp peaks to the right of $CO_2{}^+$ are at $m/q = 45, 46$ and are likely to be isotopes of $CO_2{}^+$. The width of the parent ion ($CO_2{}^+$) peak is 9 ns, corresponding to a p_z FWHM of 4.3 a.u.

can be sorted out to create a conditional distribution of another variable.

We now look at how ion momentum components are determined from the position and TOF data. Ions are dispersed in position and TOF according to their m/q and $\mathbf{p}$. The TOF spectrum brings out the dispersion in m/q as well as in p_z, whereas the position spectrum brings out the dispersion in p_x, p_y. While different ion species are identified as TOF mass peaks, the detector image is a superposition of the position spectra of all ion species. The (x, y) distribution of the ions of the chosen species is obtained by setting a window on the TOF peak of the ion species, and filtering out events with t values falling within this window. The three momentum components are obtained using the relationships:

$$p_z = (t - t_0) q E_s$$
$$p_x = \frac{(x - x_0) m}{t}$$
$$p_y = \frac{(y - y_0) m}{t}$$

here, t_0 is the centroid of the TOF peak in question, and (x_0, y_0) is the centroid of the position distribution of the parent ion (here: $CO_2{}^+$). The centroids of the TOF peaks are in linear regression with $(m/q)^{1/2}$. The first of these expressions is approximate, but the approximation is excellent provided $p_z^2/2m \ll qsE_s$, a condition well-satisfied here. It is clear from the above expressions and Eqs. (1) and (4), that $\overline{p_z^2}$ is proportional to σ_t^2, while $\overline{p_x^2}$ and $\overline{p_y^2}$ are proportional to σ_x^2 and σ_y^2, respectively. Throughout this paper, momenta will be expressed in atomic units.

The present analysis is based on dissociative ionisation of CO_2 by 1300 eV electrons, in a crossed-beams geometry. Extraction field E_s is 60 V/cm. A representative TOF spectrum is shown in Fig. 1. It is evident from the shapes of the peaks in TOF spectrum, that C^+ ions have a unimodal $|p_z|$ distribution, while the O^+ and CO^+ ions have a bimodal $|p_z|$ distribution. Similar structures in p_x and p_y can be discerned from the position distributions of these ions.

4. Analysis

Two critical points in momentum analysis are correct identification of the TOF peak extent, and correction of the background. If these are not addressed in a definitive manner, the calculation of the TOF variance as well as the transverse momentum components is prone to errors.

A commonly used method of correction of background involves obtaining a linear baseline by a least-squares fit and subtracting it from the peak, but this correction is seldom satisfactory. We employ a correction by a comparative method [13,14]. In addition to the TOF spectrum obtained when the electron beam and the gas beam cross each other, a second TOF spectrum is obtained with the gas flooding the vacuum chamber uniformly, rather than as a beam. The flowrate of the gas is kept constant in the two modes of operation. The flooded mode spectrum is subtracted from the crossed-beams spectrum after correcting for variation in the electron beam current (if any). The subtracted spectrum is taken as the true TOF spectrum. The application of the subtraction technique to momentum spectra is discussed in [11].

The setting of the mass peak limits is often subjective, but some objectivity may be brought in by fitting a line shape (usually Gaussian). We use the following method. The mass peak of interest is identified in the subtracted spectrum. A conservative window demarcating the extent of the TOF peak is set, and the p_z distribution is determined. For this chosen set of events, the position spectrum and hence the p_x, p_y distributions are extracted. Following this, the variances of p_z, p_x, p_y distributions are determined. At this stage we only have a rough estimate of the momentum extents or the kinetic energy limits and a refinement is sought by repeating the procedure with broader peak extents. As events get added, the variances of the three momentum components increase, but not at the same rate. $\overline{p_z^2}$ increases faster than $\overline{p_x^2}$ or $\overline{p_y^2}$. As the TOF peak extents are increased further, there comes a point beyond which $\overline{p_z^2}$ increases rapidly, but $\overline{p_x^2}$

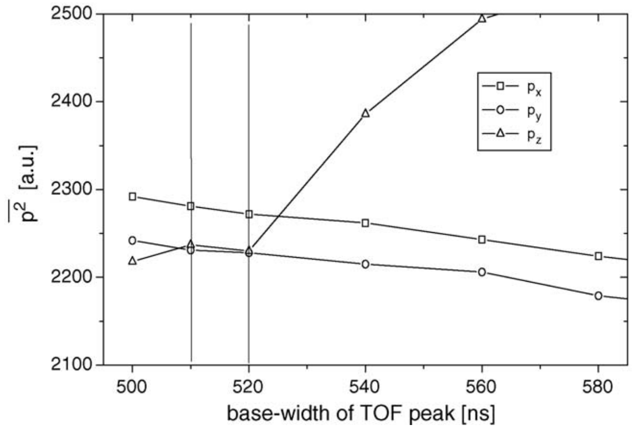

Fig. 2. Change in variance of the momentum components p_x, p_y, p_z (derived from the position (x, y) and time-of-flight (t) distributions respectively), as a function of the base-width of the TOF line for the CO^+ ion. The two vertical lines indicate margin of error in setting the base-width, when a comparison of the variances of the three components is used as a guide for setting the peak extents.

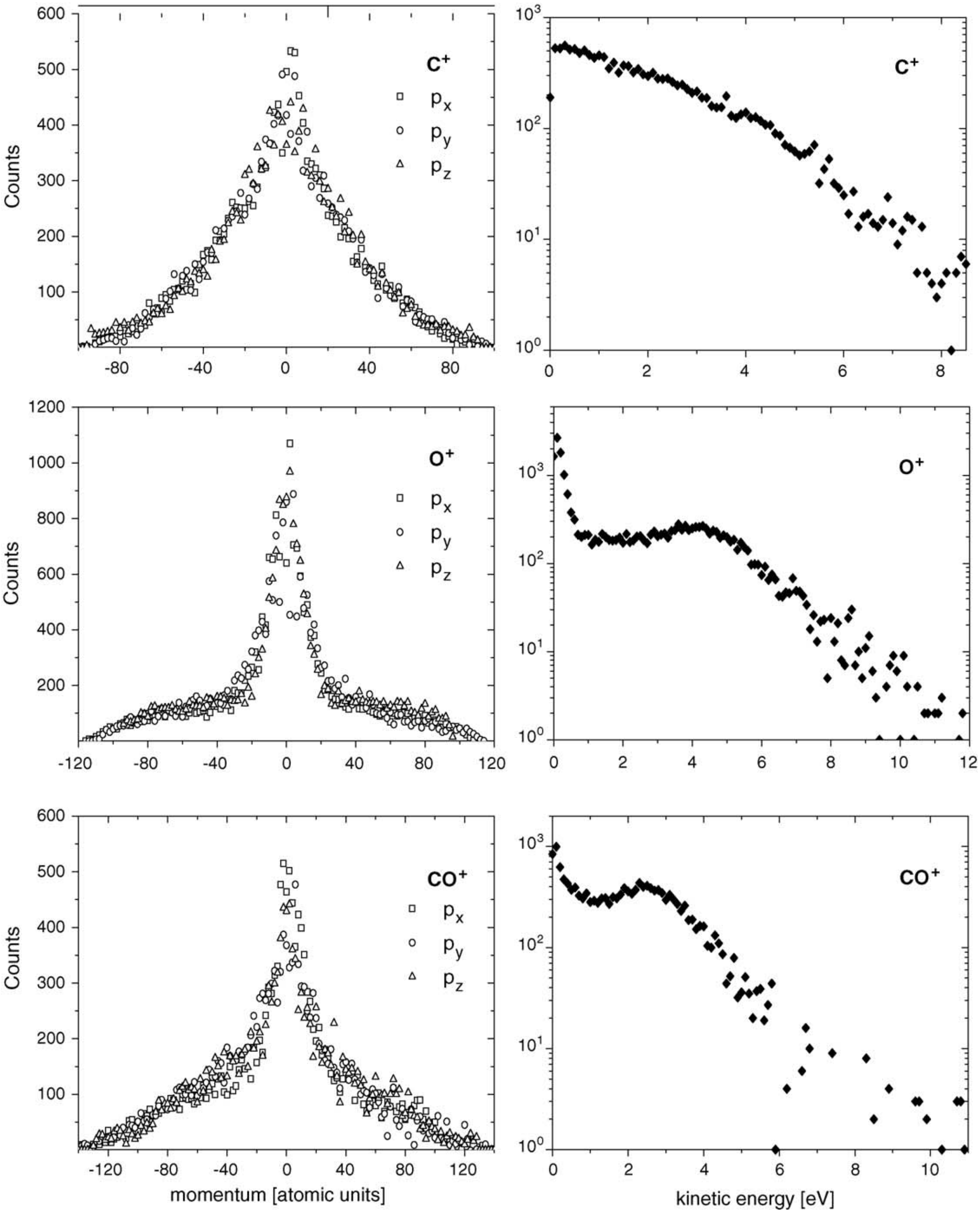

Fig. 3. *Left panel:* Distribution of the three momentum components of fragment ions C^+, O^+ and CO^+. *Right panel:* The kinetic energy distributions of the ions.

and $\overline{p_y^2}$ remain more or less constant. The contrasting behaviour of the variances of the transverse and longitudinal components is shown in Fig. 2, and indicates, with a good accuracy, the correct base-width. The contrast is due to the following reasons. Large deviations of t from the TOF centroid necessarily imply larger p_z values, but not necessarily larger p_x or p_y values. $\overline{p_z^2}$ increases because an increased extent of the TOF peak adds background events with ever larger time deviations from the centroid. On the other hand, the position distribution of these events remains restricted to the fixed extents of the detector. With unchanged limits of the x, y spread, but an increased number of events, false coincidences tend to leave the variance of the position distribution unchanged. The change in variance of p_x or p_y is typically about 1% for a change in the TOF base extent by 5%. The corresponding variation in the p_z variance can be as high as 10%.

Fig. 3 shows the distribution of momentum components for the fragment ions and their kinetic energies. It is clear, that for a particular ion species, the three momentum components are identically distributed. This isotropicity is expected, since target CO_2 molecules are randomly oriented and the momentum transfer to the target is negligible. In addition, the similarity of the distributions is indicative of the absence of discrimination against transverse emitted ions. We have ver-

Table 1
Mean-squares of momentum components and various estimates of the kinetic energies of ions

Ion	$\overline{p_x^2}$	$\overline{p_y^2}$	$\overline{p_z^2}$	$\langle K^{\Delta}\rangle$	$\langle K^{\mathbf{p}}\rangle$	$\langle K^{\sigma}\rangle$	$\langle K^{\Delta}_{\mathrm{corr}}\rangle$	$\langle K^{\mathbf{p}}_{\mathrm{corr}}\rangle$	$\langle K^{\sigma}_{\mathrm{corr}}\rangle$
C^+	1024	1072	1078	1.78	1.96	1.99	1.78	1.91	1.98
O^+	1559	1588	1557	0.70	2.17	2.16	0.70	2.12	2.15
CO^+	2281	2231	2237	1.01	1.78	1.77	1.01	1.72	1.76

Corrected KE estimates are based on the TOF linewidth of the ${CO_2}^+$ ion. KE is in units of eV, and momenta are in atomic units.

ified, that increasing the extraction voltage to 90 V/cm does not alter the distributions of the three components significantly. Thus, the spectra shown here qualify as test-bench for Eq. (4).

The kinetic energy distributions of the O^+ and CO^+ ions are bimodal. This is reflected in the pronounced wings of their TOF peaks, and for these peaks FWHM is a rather meaningless quantity. A FWHM may be prescribed for these cases in the following manner. The normalised TOF line shape is approximated by the sum of three Gaussians, one centred on the TOF centroid, and the other two shifted symmetrically from the centroid:

$$l(t) = a_1 g_1(\bar{t} = t_0; \sigma_1) + a_2[g_2(\bar{t} = t_0 + \tau; \sigma_2) + g_2(\bar{t} = t_0 - \tau; \sigma_2)]. \tag{6}$$

$a_1, \sigma_1, a_2, \sigma_2, \tau$ are obtained by a least-squares fit, following the Levenberg–Marquardt algorithm. The weighted mean of the FWHM of g_1 and g_2 is taken to be the FWHM of the entire peak:

$$\Delta t = 2(2\ln 2)^{1/2}(a_1\sigma_1^2 + 2a_2\sigma_2^2)^{1/2}. \tag{7}$$

This prescription is used in Table 1.

5. Results and Conclusions

The mean-squares of the individual momentum components and the three KE estimates are presented in Table 1. For all ions, the mean-squares of the three components are in excellent agreement with each other. The equipartition of the momentum into three components is thus clear.

The momentum based estimates and the variance based estimates are in good agreement for all ions. For no ion does the FWHM based estimate agree with other estimates. The FWHM based estimates for O^+ and CO^+ are much smaller than the variance based values, indicating that the small momentum (narrow) TOF component dominates the FWHM calculation. In contrast, the variance based estimate for these ions is in excellent agreement with the momentum based estimate. For these ions, it may be possible to deconvolve the observed distributions into two unimodal distributions, attributable to two distinct precursor states. Further on, a mean value can be assigned to each one of the two unimodal distributions. Our attempts at deconvolution were not fruitful. We note in passing, that there is very little difference between the raw and corrected FWHM based estimates, because the instrumental width, based on the FWHM of the ${CO_2}^+$ peak, is tiny.

Errors in the tabulated estimates arise from three factors. These are errors in fitting the baseline, errors in determining the peak extent, errors in mapping position and TOF information onto the momentum space. Of these, the error due to incorrect limits is about 5%, baseline corrections 2% and mapping about 2%. Thus, K^{σ} estimate has an error of about 6%, while $K^{\mathbf{p}}$ has an error of about 8%. The FWHM based estimate, however, remains nearly unaffected by these factors. It is largely determined by the goodness of fit of the Gaussian. The regression coefficients for the C^+, O^+ and CO^+ peaks are 0.90, 0.94, 0.78 respectively.

In conclusion, our analysis verifies the proposition, that the variance of the TOF distribution is a good estimate of the mean KE. Our analysis also affirms that the mean based on FWHM of a TOF peak is an under-estimate. Especially in the case of bimodal ion kinetic energy distributions, where the FWHM based estimate is not meaningful, the variance based estimate agrees with the momentum based estimate. The analysis also shows how the flooded mode spectrum is useful for correcting the baseline of the TOF peaks. The change in the variance of the TOF line as a function of the base-width of the line is suggested as an indicator of whether or not the extent of the TOF line has been correctly set. For those cases, where the transverse components of momentum are also measured, it is further shown, that one can set the extent of the TOF peak unambiguously, by comparing the TOF variance with the variance of the corresponding position distribution.

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