

## Molecular H<sub>2</sub> in intense laser fields probed by electron-electron, electron-ion, and ion-ion covariance techniques

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The techniques of electron-electron and electron-ion covariance mapping have been used to confirm that a laser of modest rise time ( $\sim 1$  ps) and focused intensity ( $\sim 10^{15}$  W/cm<sup>2</sup>) will doubly ionize H<sub>2</sub> molecules in a sequential manner. This stepwise behavior manifests itself in structureless features on the electron-electron maps. However, the technique can be employed to search for correlated emission of two or more electrons in more complex systems. Electron-ion maps, on the other hand, can apportion the electrons in a typical photoelectron spectrum to the parent ions and to fragment ions of all energies.

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When simple diatomic molecules such as H<sub>2</sub> are subjected to intense laser fields, the resulting dynamics can be extremely complex. A number of dissociation or ionization channels may be accessed, each occurring with a branching ratio depending critically upon the laser wavelength, rise time, and focused intensity. For example, resonantly enhanced multiphoton excitation may result in thermal H<sub>2</sub><sup>+</sup> ions and their associated electrons. Alternatively, rapid photodissociation may be followed by atomic ionization. At higher laser intensities resonantly enhanced dissociative ionization may occur; this may or may not be accompanied by ionization of the H atom to produce two correlated protons. The laser field may itself create transient bound states by avoided crossings [1]; this bond softening may produce additional structure in photoelectron and photoion time-of-flight (TOF) spectra. Moreover, with lasers of rapid rise time, direct non-resonant double ionization might occur, with the two simultaneously ejected electrons sharing the excess energy in a well-defined way.

Add to these competing mechanisms the structure associated with the process of above-threshold ionization (ATI) [2] and energy shifts due to the ponderomotive effect [3] and one sees that the analysis of conventional electron and ion TOF spectra is by no means straightforward. In such circumstances it is important to perform photoelectron-photoelectron, photoelectron-photoion, and photoion-photoion coincidence experiments; simultaneous acquisition of photoelectron and photoion TOF spectra is not sufficient. This Rapid Communication presents preliminary data on experiments of this type using the technique of covariance mapping [4], in essence a triple-coincidence technique applicable where pulsed excitation is used.

The covariance technique has been applied so far to the analysis of ion TOF spectra. For example, when molecules such as N<sub>2</sub> are multiply ionized by an intense picosecond laser, many tens of ions (N<sup>+</sup>, N<sup>2+</sup>, N<sup>3+</sup>) are produced per laser pulse. In the case of such homonuclear

molecules, unambiguous analysis of time-averaged TOF spectra in terms of processes such as N<sub>2</sub><sup>4+</sup>  $\rightarrow$  N<sup>2+</sup> + N<sup>2+</sup> is impossible, but covariance mapping allows unequivocal correlation of all charged fragments [5]. The technique relies on the fact that the pulse-to-pulse TOF spectra have large statistical fluctuations and if one calculates the contribution to the covariance  $C(t_1, t_2)$  between pairs of TOF spectrum points at each laser pulse [ $C(t_1, t_2) = \langle X(t_1) \times X(t_2) \rangle - \langle X(t_1) \rangle \langle X(t_2) \rangle$ , where  $X(t)$  is the detector response at time  $t$  and the average is taken over many laser pulses], then the result can be displayed in the form of a three-dimensional map showing correlations between all fragment ions.

The present experiment extends the application of the technique to electrons. A laser of wavelength 600 nm, pulse length 3 ps, pulse rate 10 Hz, and focused intensity approximately  $10^{15}$  W/cm<sup>2</sup> ionizes a beam of H<sub>2</sub> atoms. An electric field across the interaction region accelerates electrons towards one drift tube, ions towards another. The charged particles are detected by microchannel plates. An axial magnetic field ensures efficient collection of electrons and protons [6]. Since the laser is highly linearly polarized with its  $E$  vector along the axes of the two coaxial drift tubes, the electrons are ejected initially towards ("forward" electrons) or away from ("backward" electrons) the electron detector [7]. The ions are also ejected preferentially towards (H<sub>f</sub><sup>+</sup> ions) or away from (H<sub>b</sub><sup>+</sup> ions) the ion detector [8]. The design of the double drift tube is such that the forward and backward electrons and ions arrive at their respective detectors with a TOF,  $t$ , given by the formula

$$t = A \left( \frac{m}{qU} \right)^{1/2} \pm B \left( \frac{mv_{\parallel}}{qU} \right) \text{ for } \frac{mv_{\parallel}^2}{2} \leq 0.1qU,$$

where the first term represents the TOF of zero energy electrons (or ions),  $mv_{\parallel}$  is the electron (or ion) momentum component along the drift tube axis,  $U$  is the potential difference between the focal point and free drift region,

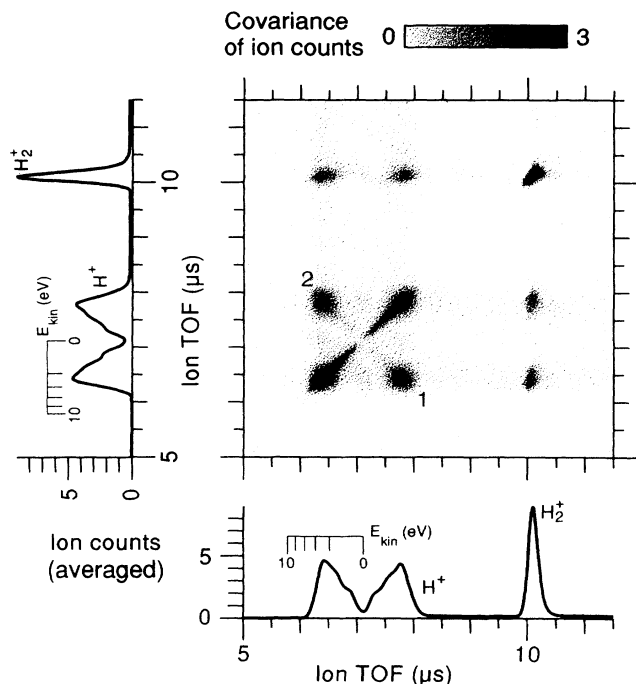


FIG. 1. Ion-ion covariance map of  $\text{H}_2$  at  $8 \times 10^{-7}$  torr ambient pressure. The features are for 1,  $\text{H}_2^+ + \text{H}^+$ ; 2,  $\text{H}^+ + \text{H}_2^+$ . The three features at  $45^\circ$  ( $t_x = t_y$ ) are parts of the autocorrelation line.

and  $A$  and  $B$  are instrumental constants (these differ for electrons and ions), Hence the electron and ion TOF spectra are symmetric about zero energy TOF and the resulting covariance features can in principle be analyzed in a rather straightforward manner.

However, one has to be quite certain that such features are not due to false correlations. This is particularly important when the physics involved leads to diffuse features on the covariance maps. To appreciate this problem we show examples of ion-ion correlations (Figs. 1 and 2), where the real and false signals are easily differentiated. This enables the use of a more elaborate procedure (Fig. 3) to establish the regime in which the electron-electron correlation maps, although diffuse in character, represent processes with real physical significance.

Figure 1 shows an ion-ion covariance map taken at an ambient pressure of  $8 \times 10^{-7}$  torr (the pressure in the  $\text{H}_2$  beam is about twice as high), using 11000 laser pulses. Alongside the  $x$  and  $y$  axes is placed the conventional time-averaged ion TOF spectrum. The circular shape of features 1 and 2 (see Fig. 1 caption) suggests an artifact due to laser fluctuations, indicating too high a count rate, or gas pressure. Additional features on the map, implying impossible correlations between  $\text{H}^+$  and  $\text{H}_2^+$  ions, confirm this fact. Figure 2 shows a map taken at a much reduced pressure of  $2.4 \times 10^{-8}$  torr but with otherwise identical conditions. Here the spurious features have disappeared (only the noise remains) and the  $45^\circ$  line, at  $t_x = -t_y$ , shows the real correlated features. A scan along the  $45^\circ$  line indicates three peaks either side of the autocorrelation line, associated with protons of kinetic energies 0.35, 1.4, and 2.4 eV. We note that these peaks are

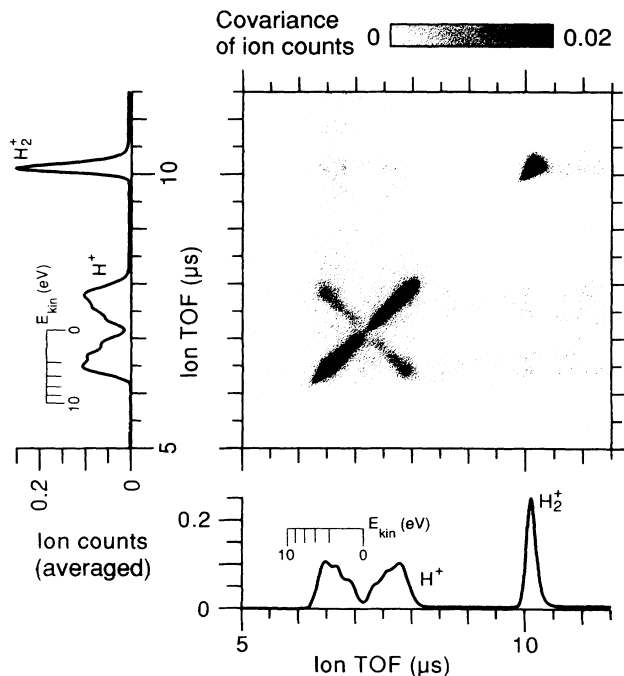


FIG. 2. Ion-ion covariance map of  $\text{H}_2$  at  $2.4 \times 10^{-8}$  torr.

separated by 1 eV or half the photon energy. What is most probably being observed here is above threshold dissociation [1] or bond softening [9]. Such structure was seen but not recognized in an earlier publication on  $\text{H}_2$  [8].

In order to ascertain the range of pressure over which meaningful results could be obtained, a series of ion-ion, electron-electron, and electron-ion maps were produced, along with the conventional TOF spectra. An average count per time channel in the peak of the electron and proton TOF spectra is plotted, Fig. 3, curve  $a$ , as a function of ambient pressure. The log-log plot produces a

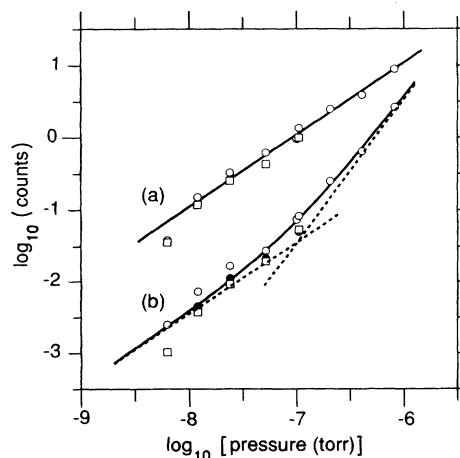


FIG. 3. (a) Average counts per TOF channel vs ambient pressure from proton TOF spectra ( $\circ$ ) and electron TOF spectra ( $\square$ ). (b) Average counts on covariance map vs ambient pressure from ion-ion maps ( $\circ$ ), electron-electron maps ( $\square$ ), and electron-ion maps ( $\bullet$ ).

straight line of unit slope, as expected. In Fig. 3, curve *b*, the average counts associated with the strongest feature on the electron-electron, electron-proton, and proton-proton maps are plotted. The dashed lines indicate a slope of 1 expected for the true signal and a slope of 2 expected for the false signal due to laser fluctuations (proportional to the square of the gas pressure). The solid line, which is the sum of the two, fits the data very well and suggests that if an excessive false contribution is to be avoided, a maximum gas pressure of no more than  $10^{-7}$  torr should be used.

Figure 4 shows an electron-ion covariance map at a pressure of  $2.4 \times 10^{-8}$  torr, with the time-averaged electron and ion TOF spectra shown, for convenience, on the *x* and *y* axes. The electron TOF is virtually structureless, the slight forward-backward asymmetry and the peak in the backward TOF spectrum at 292 ns being due to a small inhomogeneity in the extraction field. The forward electrons are unaffected by this field inhomogeneity and a kinetic-energy scale is shown for both electrons and protons. In order to ensure that this lack of real structure was not the result of poor instrumental resolution, an electron TOF spectrum of Xe was taken under identical conditions. Figure 5 shows ATI peaks in both the forward and backward spectrum, separated by the photon energy of about 2 eV; the shape of the features reflects the time resolution of the detector system of about 2 ns.

Figure 4 therefore shows at a glance, and definitively, the photoelectron spectra associated with thermal  $\text{H}_2^+$  ions and with  $\text{H}^+$  ions of all energies, that is, with the nondissociative and dissociative ionization channels. With the modest resolution implied by Fig. 5 one would not expect to see vibrational structure in the photoelectron spectrum associated with  $\text{H}_2^+$ , as observed at lower laser in-

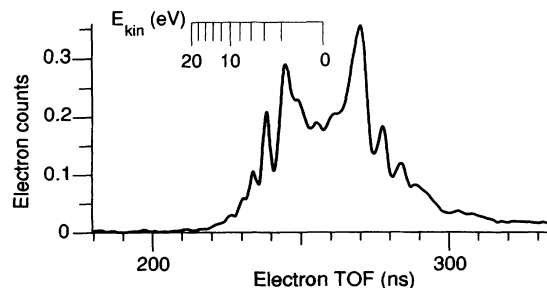


FIG. 5. Photoelectron spectrum of Xe.

tensities [10], and the poor signal-to-noise ratio precludes the observation of structure in the photoelectron spectra associated with the  $\text{H}^+$  ions. All that one can say is that the photoelectrons associated with  $\text{H}_2^+$  ions have a more restricted energy range than those associated with  $\text{H}^+$ .

Figure 6 shows an electron-electron covariance map at the same pressure of  $2.4 \times 10^{-8}$  torr. The map is featureless; there are no obvious correlations between the electrons. (The broad stripes at  $45^\circ$  are artifacts produced by electronic ringing.) This lack of structure is in contrast to the ion-ion map, Fig. 2, where the localized nature of the features indicates that the protons are ejected with quite well-defined energies and along the laser *E* field. This restricted angular spread was noted in an earlier publication [8]. The protons will necessarily share their energy of dissociation equally but no particular energy sharing is evident in the case of the electrons, nor are there any clear angular correlations between the two outgoing electrons. This is, perhaps, to be expected because the ionization process is sequential rather than direct.

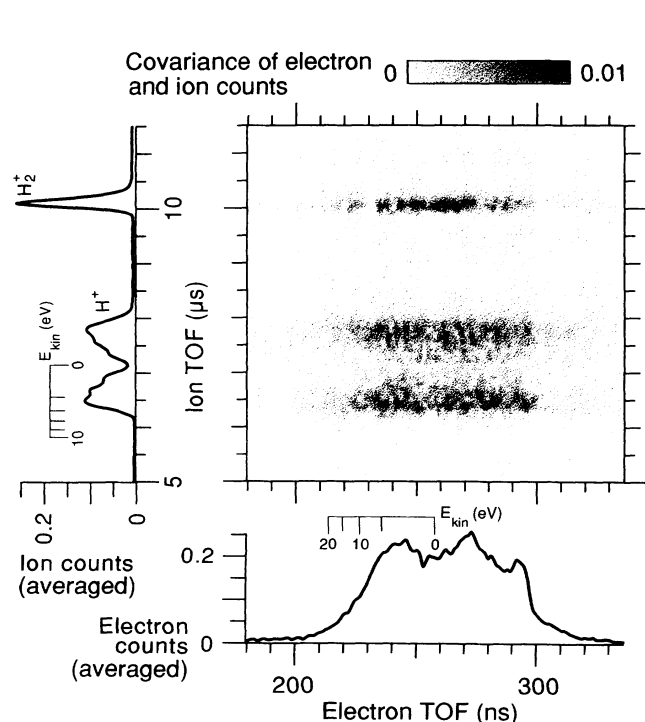


FIG. 4. Electron-ion covariance map of  $\text{H}_2$  at  $2.4 \times 10^{-8}$  torr.

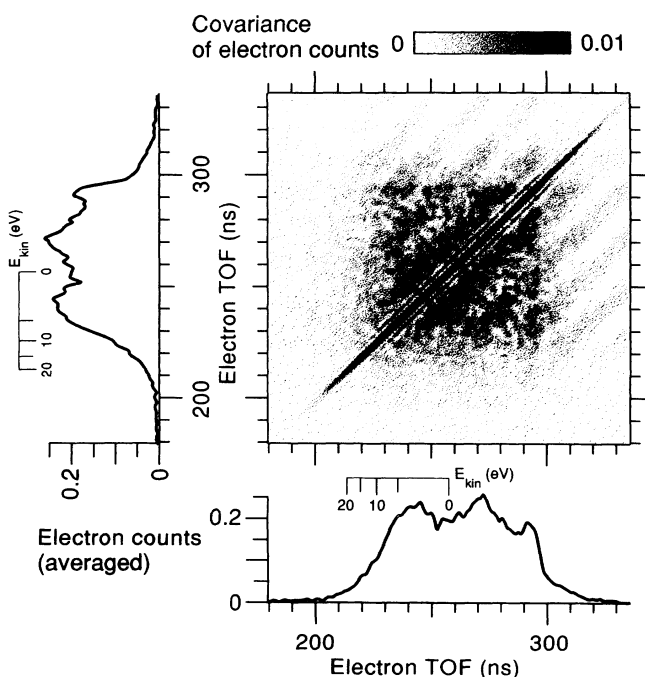


FIG. 6. Electron-electron covariance map of  $\text{H}_2$  at  $2.4 \times 10^{-8}$  torr. This map and Figs. 2 and 4 were obtained using the same raw data.

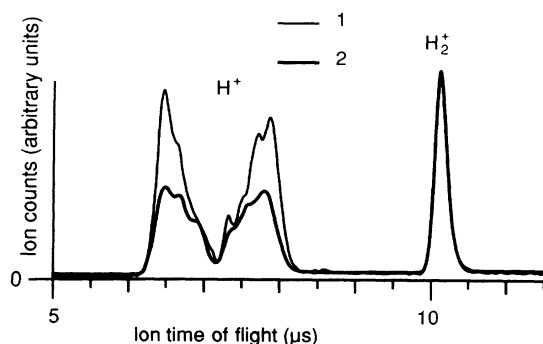


FIG. 7. Ion TOF spectrum of  $H_2$ . Line 1 is from the electron-ion map and line 2 is from the conventional ion TOF spectrum, (Fig. 4).

The low proton energies seen in Fig. 2, peaking at 2.4 eV and with a maximum at about 6 eV, confirm that sequential ionization is indeed the dominant process. If direct, nonresonant double ionization were to occur, the protons would have a peak energy of 10 eV and range from about 8 to 13 eV [8]. Such a direct process would only be expected if a laser of a much shorter rise time was employed.

One can determine the relative probabilities of single and double dissociative ionization by comparing the conventional ion TOF spectrum and the ion TOF spectrum produced by projecting all ions appearing on the electron-ion map, Fig. 4, onto the  $y$  axis. Figure 7 shows the two ion spectra normalized to the same  $H_2^+$  peak height. If the two  $H^+$  curves had been the same, this would indicate that all processes result in  $H^+ + H$ . This is simply because one electron is emitted in this process and in the normalizing process. If the  $H^+$  curve from the map had been double the height of the conventional TOF spectrum, the conclusion would be that all processes lead to  $H^+ + H^+$ . In fact one sees that, in general, the low-energy  $H^+$  ions are the result of the former process and the high-energy  $H^+$  ions are the result of the latter. More importantly, one can apportion the various  $H^+$  ions to the two processes.

Further useful information can be derived from Figs. 2 and 6, the ion-ion and electron-electron maps. By projecting all ion counts on the ion-ion map onto the  $x$  axis and comparing this with the conventional ion TOF spectrum or by projecting all counts on the electron-electron map onto the  $x$  axis and comparing this with the conventional electron TOF spectrum one can obtain a measure of the relative contributions of single and double ionization.

The question remains as to the specific routes to double ionization. Is dissociation followed by ionization of both H atoms or is dissociative ionization followed by ionization of the remaining H atom? To answer this question the photoelectron spectrum associated with each group of ions must be studied in detail. In this first electron-ion covariance experiment the signal-to-noise ratio of the map, Fig. 4, is not good enough to warrant such a procedure. Moreover, the underlying sequential processes result in electrons that are uncorrelated in momentum or angle and this leads to an unstructured electron-electron map, Fig. 6. However, one can envisage situations, with different lasers or different molecules, where particular dissociation or ionization channels produce a continuum of energies from correlated electrons. Such channels would be *impossible* to recognize in a conventional electron TOF spectrum, but possible to observe as isolated features on an electron-electron map. These features would appear as circular rings, for example, if two electrons shared a specific excess energy in a random fashion and were emitted along the laser  $E$  field. Alternatively, one can expect cases where two or more competing processes produce electrons with discrete but very similar energies. Only by using electron-ion covariance can these electrons be unambiguously associated with ions of specific energy and charge-to-mass ratio.

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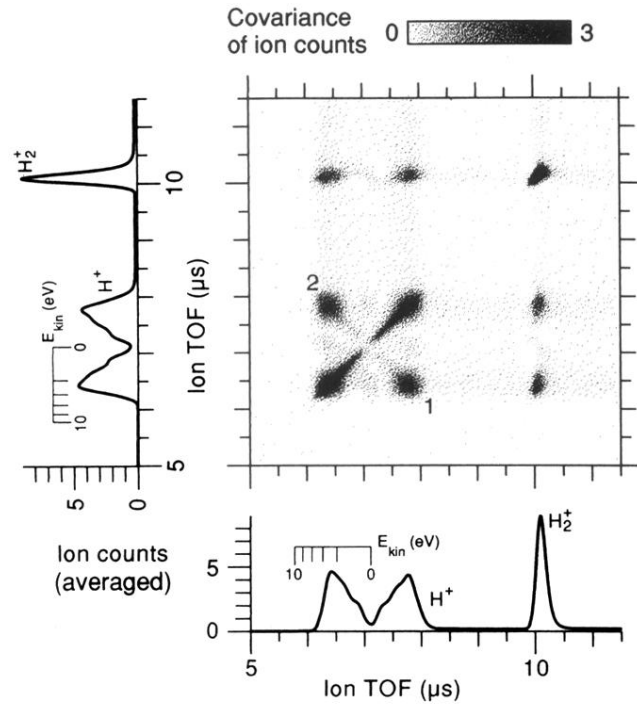


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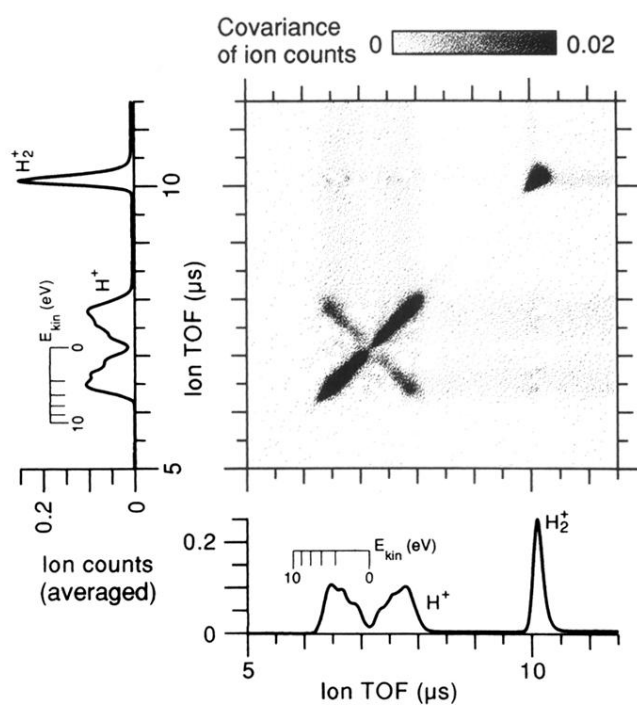


FIG. 2. Ion-ion covariance map of  $\text{H}_2$  at  $2.4 \times 10^{-8}$  torr.

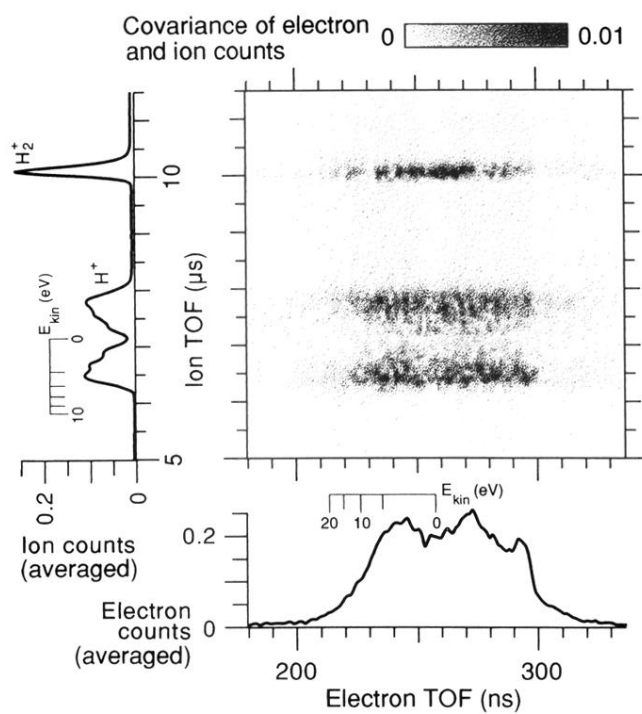


FIG. 4. Electron-ion covariance map of  $\text{H}_2$  at  $2.4 \times 10^{-8}$  torr.

