

LETTERS TO THE EDITOR

The Letters to the Editor section is divided into three categories entitled Notes, Comments, and Errata. Letters to the Editor are limited to one and three-fourths journal pages as described in the Announcement in the 1 January 2001 issue.

NOTES

Comment on the accuracy of absolute electron-impact ionization cross sections for molecules

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Electron-impact ionization of molecules is of fundamental importance in many areas of science and technology and has been the subject of numerous experimental studies over the last seventy years or so. These studies fall into two general classes, those in which the cross sections for total charge production are determined and those in which the partial cross sections for the various product ion species are measured. Of these, the determination of total cross sections is a much simpler task and agreement between the results of various laboratories is often quite satisfactory. The absolute measurements of Rapp and Englander-Golden¹ are perhaps the most comprehensive. They have been widely accepted as the *de facto* standard and have been utilized by numerous investigators to normalize their relative cross section data. Determination of the partial cross sections for the various product ions is a far more difficult task and requires the use of a mass spectrometer. The published partial cross section data are in considerable disarray, in large part because of difficulties in ensuring complete collection of the fragment ions which are often formed with appreciable kinetic energy. In consequence there is no agreement as to the correct values for many of these cross sections, since each successive study has often merely added another set of numbers to the existing array. The different measurements often do not agree with one another to within the stated uncertainties and often have quite different energy dependencies. Comparison of the results of any two laboratories reveals that while they may agree for one molecule, for another molecule the results may be entirely different. In these circumstances clearly one or perhaps both sets of measurements are inaccurate and there is no logical way to determine which of the conflicting data are correct. What is needed to resolve this impasse is an array of independent absolute cross sections from two different laboratories which are in complete agreement, since while it is possible for two laboratories to exhibit identical yet incorrect results for a large number of molecules, such an eventuality would seem highly improbable.

A few years ago an apparatus was developed in this laboratory for the specific purpose of determining highly accurate independently absolute partial electron-impact ionization cross sections for atoms and molecules. The experimental technique involves passing a pulsed electron beam through a static gas target, then extracting, mass analyzing and counting the ions formed along a known path length.^{2,3} It embodies the simplicity of the parallel plate arrangement used by Rapp and Englander-Golden¹ coupled with an extremely short path length mass spectrometer together with a detector with which it is possible to demonstrate complete collection of all fragment ions. This approach overcomes many of the limitations of other techniques and should be capable of providing very accurate absolute partial cross sections.

A number of publications have resulted from this work and in every case the total cross sections, obtained as the sum of the partial cross sections, was found to agree with the results of Rapp and Englander-Golden.¹ While such individual comparisons are useful, they have not enabled the overall picture to emerge and in this paper a comparison is made of the cross sections for all molecules studied both in this laboratory and by Rapp and Englander-Golden.¹ Figure 1 provides that comparison for H₂, N₂, CO, CO₂, CH₄, and SF₆. The data of Rapp and Englander-Golden¹ are actually for total charge production, whereas the present data are the sums of the partial cross sections which were obtained by counting the number of product ions of each species. Because only very few multiply charged ions are observed these two cross sections are, however, essentially identical. Agreement between the two sets of data, both of which have uncertainties in the $\pm 5\%$ – 7% range, is clearly excellent in every case. The only other molecular targets for which both laboratories have published cross sections are O₂ and NO. For these gases, Rapp and Englander-Golden¹ experienced particular difficulties and their data were accordingly reported as estimates. Nevertheless, the two sets of data again

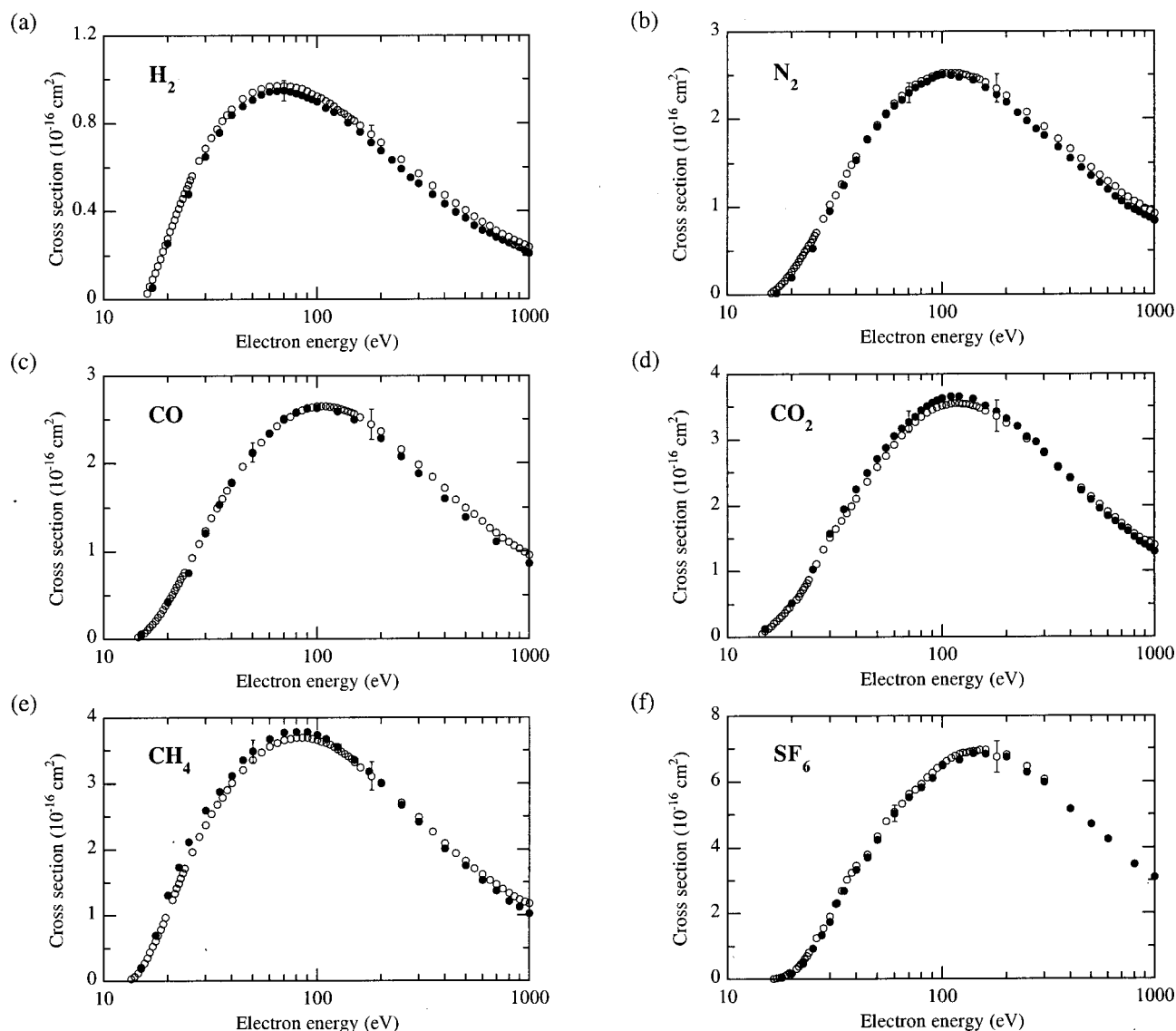


FIG. 1. Total electron-impact ionization cross sections for H_2 , N_2 , CO , CO_2 , CH_4 , and SF_6 : present results (Refs. 3, 5–9) (●); Rapp and Englander-Golden (Ref. 1) (○). The slight tendency of the Rapp and Englander-Golden (Ref. 1) data to be high at energies greater than 400 eV or so may be due to incomplete collection of the electrons at these energies (Ref. 10).

agree to within the combined uncertainties although the agreement is clearly not as good as for the other targets (Fig. 2). Excellent agreement is also observed between the data from this laboratory and that of Rapp and Englander-Golden¹ for all five rare gases.⁴ Thus for all 13 gases studied both by Rapp and Englander-Golden¹ and in this laboratory the results are in complete accord. This level of agreement between the measurements from two laboratories is perhaps unprecedented and would seem to justify a high level of confidence in them. This result therefore essentially validates the widespread adoption of Rapp and Englander-Golden's¹ measurements.

Perhaps of even greater significance is the implication this result has for the correctness of the partial cross sections determined in our laboratory. An important aspect of our experimental arrangement is that the signals for all product ions are determined simultaneously, rather than sequentially. The possibility of error in the relative magnitudes of the

various partial cross sections due to electron current, pressure or other instrumental instabilities is therefore effectively eliminated. Furthermore, it has been demonstrated that all product ions are detected with the same efficiency irrespective of their mass or initial kinetic energy. It is evident therefore that the ratios between the various partial cross sections are determined with very high accuracy, higher in fact than that with which the absolute values themselves are determined. These considerations provide strong support for the accuracy of the measured partial cross sections since there appears to be no conceivable way in which both their sum and the ratios between them could be measured correctly without the partial cross sections themselves being individually correct. It would appear therefore that the work of Rapp and Englander-Golden¹ together with the work from this laboratory leads to the correct values of both the total and the partial cross sections for electron-impact ionization of these molecules.

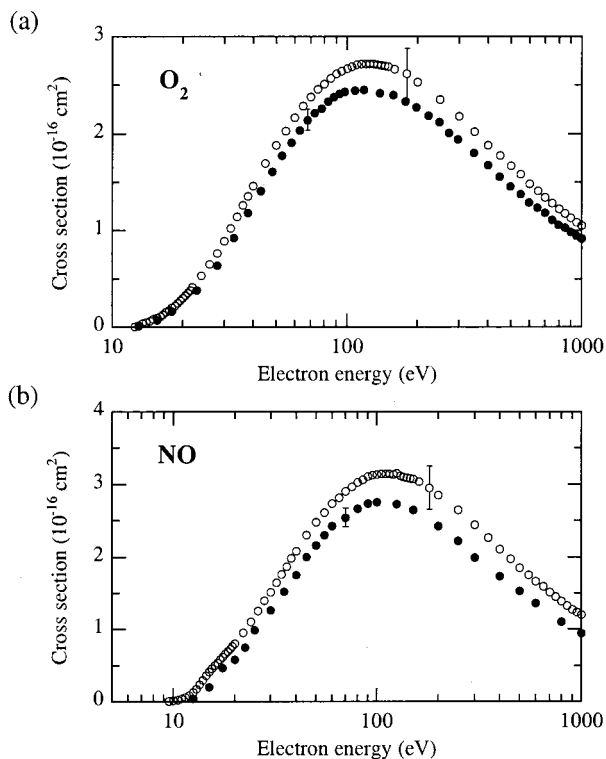


FIG. 2. Total electron-impact ionization cross sections for O_2 and NO : present results (Refs. 3, 11) (●); Rapp and Englander-Golden (Ref. 1) (○).

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- ⁹Note that the present data for H_2 , N_2 , O_2 , CO_2 , and CH_4 reflect a recent recalibration of the apparatus and differ slightly from those in the original publications. The updated values have been tabulated by B. G. Lindsay and M. A. Mangan, in *Landolt-Börnstein, I/17C: Photon- and electron-interactions with molecules: Ionization and dissociation*, edited by Y. Itikawa (Springer-Verlag, Berlin-Heidelberg) (to be published).
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