W, F, and I: Three Quantities Basic to Radiation Physics

Mitio Inokuti

Physics Division, Argonne National Laboratory, Argonne, Illinois 60439, U. S. A.

Prologue

A topical area of Professor Doke's recurring work concerns physical quantities basic to radiation physics and dosimetry. Therefore, I believe it appropriate to dedicate to him with sincere respect the present essay reporting on the current status of understanding of the most fundamental three listed in the title. Throughout I will focus on the physical meanings of these quantities and their magnitudes, considered from the structure of atoms, molecules, and their aggregates, viz., condensed matter, with minimal reference to technical details.

1. W

1.1. Background

The W value is an index of the mean number of ions produced in a gas subjected to ionizing radiation. Formally, it is defined as the radiation energy absorbed (usually expressed in units of eV) "per ion pair of either sign produced", or, in a simpler language, "per electron liberated". The basic knowledge up to 1961 is eloquently articulated in a classic essay by Platzman [1], which Professor Doke loves to cite. The theme of Platzman was to explain from the point of view of basic physics the magnitude and characteristics of the ratio W/I, where I is the (first) ionization threshold energy. In summary, major characteristics are as follows.

1) The W value for a given gas depends weakly on the properties of the radiation such as the mass and charge of particles or initial energies (provided they are sufficiently

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high). This makes the ionization measurement useful as a method of dosimetry, viz., the determination of the absorbed energy.

2) The ratio W/I is always greater than unity because a part of the absorbed energy must be used in nonionizing events such as discrete excitation or molecular dissociation into neutral fragments and also in producing subexcitation electrons, viz., electrons with kinetic energies too low to cause electronic excitation or ionization [2].

3) The ratio W/I is 1.7-1.8 for rare gases, and 2.1-2.6 for gases of common molecules (depending on the electronic structure, going from "hard" to "soft").

Calculation of the W value is possible from three approaches: i) the energy balance of Platzman, heuristic for general understanding and appropriate for an estimate; ii) the Fowler equation [3] for the direct evaluation of the mean number of ions produced; and iii) the method of Spencer and Fano [4] through the degradation spectra (or the track length distributions) of charged particles, most importantly of electrons, present in the medium. The Fowler method is good for obtaining the mean number of ions or excited states resulting from the incidence of particles of relatively low energies, while the Spencer-Fano method is good for the incidence of high-energy particles.

The Spencer-Fano method is informative in showing the relative importance of ranges of different particle energies, in the form of the yield spectrum, as explained below. Consider a gas consisting of n molecules per unit volume of a single chemical species. Let $\sigma_i(T)$ be the total ionization cross section of the molecule by an electron of kinetic energy T. During its passage over an infinitesimal path length dx, the electron produces the number of ion pairs (more precisely, of liberated electrons) expressed as $dN_i = n \, \sigma_i(T) \, dx$. Thus the total number of ion pairs is given by the integral

$$N_i = n \int \sigma_i(T) \, dx \tag{1}$$

over the total path length. If one may regard x and T as related by a well defined smooth function, then one may write $dx = (dT/dx)^{-1} dT$ and carry out the above integration, where dT/dx is the mean energy loss per unit path length, viz., the stopping power. This

treatment is called the continuous-slowing-down approximation (CSDA), and is justified if most of the energy losses on individual collisions are much smaller than the current kinetic energy T, as is nearly the case for a heavy charged particle at high speeds. However, the CSDA is inadequate for electrons in general because the energy loss of an electron can be as high as $(T - I)/2$, which occurs on a head-on collision, and also because the CSDA cannot account for the production of secondary electrons.

Spencer and Fano [4] in effect wrote $dx = y(T)\, dT$, introducing the electron degradation spectrum, or the track length distribution, $y(T)$ and deriving an integral equation for $y(T)$. Under stationary irradiation, $y(T)\, dT$ means the total path length of all the electrons present in the medium having kinetic energies between T and $T + dT$. Then, Eq. (1) becomes

$$N_i = n \int \sigma_i(T)\, y(T)\, dT. \tag{2}$$

In general T ranges from several eV up to keV or even MeV, and therefore it is sensible to consider $\ln T$ as an independent variable and to rewrite Eq. (2) as

$$N_i = n \int T \sigma_i(T)\, y(T)\, d(\ln T). \tag{3}$$

Indeed, $\ln T$ represents, apart from a constant factor, the mean number of elastic collisions that reduces T by a constant fraction, if the scattering is isotropic and independent of T. (In neutron slowing-down theory [5], $\ln T$ is a key variable called the lethargy.) We may call the integrand $T \sigma_i(T)\, y(T)$ the yield spectrum, which represents the contribution to the total number of ion pairs from a unit range of $\ln T$. Interestingly, the product $T \sigma_i(T)$ is the same within a proportionality constant as the collision strength, a quantity more fundamental than the cross section in the general collision theory [6], and is also useful in the context of the Bethe theory [7].

An example of the yield spectrum is seen in Fig. 1, reproduced from Inokuti et al. [8]. The contribution to the yield of ions (or of excited states accessible from the ground state by dipole-allowed transitions) from each unit range of $\ln T$ is roughly the same, except for markedly greater contribution near the source kinetic energy; for instance,

the range 100-200 eV contributes roughly the same as the range 200-400 eV, 400-800 eV, and so forth.

1.2. Recent Developments

Data on the W values of gases (as well as of corresponding quantities for semiconductors) are reviewed in ICRU Report No. 31 [9], and more recently in Chapter 8 of an IAEA report [10].

Since the mid-1970s I have studied the evaluation of the yield of ions or excited states from various angles together with many co-workers, as seen in a review article [11], which concentrates on the most fundamental case of electron incidence, and in Inokuti et al. [12], which treats ion incidence. Main findings are as follows.

1) For the same set of cross-section data, the method of Fowler and the method of Spencer and Fano lead to the same result. Indeed, these two methods represent two alternative mathematical pictures of the same physics [13].

2) The systematics of the W value has been explored more broadly. For vapors of atoms from hydrogen to argon, approximate estimates of the W values were made [14] with the use of simple procedures [15, 16] and of theoretical oscillator-strength spectra [17] and other data. Figure 2 shows the results. The W value attains prominent maxima for fully closed shells (He, Ne, and Ar), and secondary maxima for nominally closed subshells (Be and Mg). This behavior is similar to that of the ionization threshold energy I. As Fig. 3 shows, the ratio W/I ranges from about 1.5 to about 3. It tends to be smallest for atoms near the rare gases. This trend is understandable because for these atoms a major fraction of the oscillator strength lies at high excitation energies in continua. The ratio W/I attains maxima for Be and Mg, in which the oscillator strength is large for the lowest discrete excitation (viz., the resonance transition), and modest for continua. This trend roughly explains the large measured value [18], $W/I = 2.27$ for Hg, an atom in the same column of the periodic table

3) Another systematics of the W value concerns hydrocarbons [19, 20]. For linear alkanes C_nH_{2n+2}, for instance, the W value for high-energy electrons decreases with increasing number n of carbon atoms, but with an oscillatory trend, as seen in Fig. 4. Calculations [20] indicate that the main contributor to the oscillatory variation is the branching ratio of dissociation into neutral fragments to ionization from super-excitation [21-23]. From the point of view of electronic structure, the decreasing trend of W with increasing n is qualitatively understandable. For lager and larger n, valence electrons tend to be less and less localized, as the ionization threshold I indeed indicates; however, I shows only a minute hint of an oscillatory behavior superimposed on the decreasing trend. It remains obscure why W shows the clearer oscillatory trend.

4) Both the Fowler method and the Spencer-Fano method have been generalized to treat a mixture rather than a chemically pure substance. Results thus obtained have clarified the dependence of the yield of ions or excited states on the composition. This dependence is in general nonlinear because of a correlation in the sense that an electron responsible for producing an ion or an excited state may have resulted from ionization of any of the mixture components [24-26]. The dependence of the degradation spectrum of electrons on the composition turns out to be a rich subject of study [27].

5) The Spencer-Fano method was originally formulated to treat a time-independent case under stationary irradiation. It has now been extended to deal with time-dependent cases [28], and has proved useful for interpreting results of some gas-phase pulse radiolysis experiments [29, 30]. For instance, the production of ions or excited states accessible from the ground state by dipole-allowed transitions by a short-pulse irradiation grows linearly in time at the beginning, and eventually reaches a plateau; in contrast, the production of an excited state inaccessible from the ground state by a dipole-allowed transition begins after a period during which electrons slow down to sufficiently low energies at which the cross section for the production is appreciable.

6) The Spencer-Fano method has been applied to subexcitation electrons [29-38], viz., electrons whose kinetic energies are below the lowest electronic-excitation threshold of the major component molecule in the medium and which therefore can lose kinetic energies very gradually to the translational, rotational, and vibrational degrees of freedom. The smallness of the fractional energy loss per collision often permits one to make a simplified treatment, viz., the continuous-slowing-down approximation, or the Fokker-Planck approximation.

7) At kinetic electron kinetic energies approaching or comparable to the thermal energy of medium molecules, one must take into account not only the energy loss but also the energy gain of an electron from a molecule [39-45]. An eventual balance between the loss and gain of energy signifies thermal equilibrium. In a low-density medium such as gas at modest pressure in weak electromagnetic fields if any, one may use the Boltzmann equation, or its Fokker-Planck approximation.

1.3. Outlook

As the above summary indicates, we have now a fair understanding about principles that govern W values in general, and also about their numerical magnitudes for common gases. For better understanding of the basics, I wish to see work in the two following directions. First, the quantum yield of ionization, viz., the probability of ionization of a molecule when it has received a fixed excitation energy (exceeding the first ionization threshold I) has been extensively studied [22, 23] since Platzman [21] pointed out the importance of the topic. The oscillatory behavior [19, 20] of the W value for hydrocarbons as a function of the carbon number is certainly related to the topic. However, consequences of the quantum yield of ionization (being appreciably less than unity over a spectral range for molecules in general) to radiation effects have been only partially understood.

Second, the most fundamental object of study for the understanding of the yields of ions and excited states is the degradation spectra of charged particles (most importantly of electrons). Many calculations have been carried out to reveal main characteristics of the degradation spectra. Experimental studies on this topic were pioneered by Birkhoff [46] and co-workers; and many valuable results and insights were obtained, as seen in Ritchie et al. [47]. However, this line of work was unfortunately terminated; renewed work toward measurements of degradation spectra in various materials by use of current techniques will be most valuable. Indeed, the work by Birkhoff and co-workers concerned with solid conductors. An extension to liquids, insulators, and gases would be challenging and yet highly desirable.

Our understanding about the ionization yield is also fair for semiconductors [9], but is severely limited for other kinds of condensed matter, notably liquid [10].

2. F

2.1. Background

The yield of ionization expressed by the W value represents the *mean* number of ion pairs produced as determined by many measurements. The precise number of ion pairs (or liberated electrons) observed in each measurement at a fixed absorbed energy is *stochastic*, viz., not uniquely fixed but subject to statistical fluctuations. The fluctuations occur because the detailed history of individual ionization and excitation events is not unique but diverse. Fano [48] pioneered in the theory of this topic, and showed that the variance V_i (or dispersion, viz., the square of the standard deviation) of the number of ion pairs may be expressed in general as the product of the mean number N_i of ion pairs and a dimensionless factor F, which should depend on the material and should be less than unity. This factor, now called the Fano factor, determines the ultimate theoretical limit of precision of the radiation-energy determination by ionization measurements.

If the probability of producing an ion pair upon a collision is minute and depends on nothing else, then the precise number of ion pairs produced after many collisions should obey the Poisson statistics and F should be unity. This is indeed the case when the kinetic energy T of an incident electron is close to the ionization threshold I; then the probability of producing an ion pair is the ratio of the ionization cross section to the total inelastic-scattering cross section, and it does tend to zero as T approaches I. More generally, the ion-pair production is not described by the Poisson statistics, because the absorbed energy must be shared by ionization and excitation events; a part of the absorbed energy goes into the kinetic energies of subexcitation electrons also. Thus, the energy conservation restricts the variety of the detailed history of those events. Consequently, the statistical fluctuations in the number of ion pairs produced are restricted, leading to a smaller variance, viz., to F less than unity. When the initial kinetic energy of an incident charged particle is very high (i. e., much higher than I), F tends to a constant value, which may be regarded as a property of the material.

2.2. Recent Developments

1) Current data on the Fano factor of gases (and also for semiconductors) are reviewed in ICRU Report No. 31 [9], and in Chapter 8 of the IAEA report [10]. A recent survey of data on rare gases and their mixtures is found in Krajcar Bronic [49]. As seen in many papers cited in the report [10], Doke and co-workers contributed much, indeed more than any other single group in recent years, to the measurements of the Fano factor.

2) Progress in theory [11] may be summarized as follows. The variance V_i of the number of ion pairs can be expressed as an integral similar in form to Eq. (2) for the mean N_i of the number of ion pairs, viz.,

$$V_i = n \int \rho_i(T) \, y(T) \, dT = n \int T \rho_i(T) \, y(T) \, d(\ln T). \tag{4}$$

Here $y(T)$ is the same degradation spectrum as in Eq. (2), but $\rho_i(T)$ represents a new quantity

$$\rho_i(T) = \Sigma_k \, \sigma_k \, (T) \, [\Delta N(T)_k]^2, \tag{5}$$

where $\sigma_k(T)$ is the cross section for a collision of kind k (ionization or discrete excitation, further classified in terms of energy transfer in the collision) of an electron of kinetic energy T, and $\Delta N(T)_k$ is the increase in the mean number of ion pairs due to that collision [8]. Figure 5 shows an example illustrating the integral in the same form as the yield spectrum (shown in Fig. 1). Thus we see that the variance V_i receives contributions from different T similarly to the mean N_i except at T close to I.

The Fano factor $F = V_i / N_i$ can be expressed as

$$F = \int \rho_i(T) \, y(T) \, dT / \int \sigma_i(T) \, y(T) \, dT. \tag{6}$$

There must be a value T^* in the same interval of the two integrals, which covers the range of the kinetic energies of all the electrons present in the medium, according to Cauchy's generalized mean-value theorem [50]. The value of T^* depends on $y(T)$. However, if the ratio $\rho_i(T)/\sigma_i(T)$ varies slowly on T, then the precise value of T^* is immaterial. This is indeed generally the case, as illustrated in Fig. 6, except at T close to I. Indeed the plateau value of the ratio attained around $T = 500$ eV represents the value of F for high-energy electrons.

Furthermore, new indices characterizing in greater detail the stochastics of ionization, which may be called generalized Fano factors, have been identified and their relations with the degradation spectrum have been found [8].

3) By far the most notable discovery in recent years is the close correlation between F and W, which may be called the Krajcar-Bronic relation [51]. It is an empirical relation

$$F = a \, (W/I) + b, \tag{7}$$

approximately obeyed by data on many materials, where a and b are constants. Furthermore, these constants are nearly universal for many materials for which data are available: $a = 0.188$ and $b = -0.15$, seen in Fig. 7. The relation is extremely valuable as a guide for estimating F for a material for which W/I is known. A similar linear relation

holds closely for F and W for binary mixtures of varying composition, as illustrated in Fig. 8.

From a basic point of view, the Krajcar-Bronic relation is qualitatively understandable in the following way. When W/I is small, many ions are readily produced; this means that many ionizing collisions, as well as many nonionizing collisions, occur; this in turn means that the history of individual collision processes is certainly diverse but is subject to the energy conservation. Therefore, F should be appreciably less than unity. When W/I is large, a modest number of ions are produced as a result of a modest number of collision processes; then, the energy conservation is less relevant, and therefore F should be large (within the general limit F being less than unity). In summary, F and W/I should go together when one looks at different materials. However, it has been difficult to explain fully why the linear relation fits so closely a bulk of data and how the almost universal values of a and b arise.

4) An important development concerns a difference of the Fano factor for the incidence of different particles. Doke and co-workers [52] reviewed experimental data, reported in the literature as well as their own [53-55], and pointed out that the Fano factors of rare gases and their mixtures for α particles are clearly larger than those for electrons. In argon, for example, F is about 0.16 for high-energy electrons, and about 0.20 for α particles. Notably, most of theoretical results on the Fano factor so far reported concern the incidence of electrons, and generally agree with experimental results for electrons.

Doke and co-workers [52] attribute the larger Fano factor for α particles to the contributions of "nuclear" elastic collisions of α particles with atoms leading to energy transfer to the translational motion, as earlier discussed by Lindhard and Nielsen [56]. This idea is certainly plausible, because the nuclear elastic collisions add to the diversity of the detailed history of elementary collision processes, causing an increase in the Fano factor. Calculations by Inokuti et al. [12], who failed to include this contribution, led to

the Fano factor of argon for protons nearly the same as for electrons of the same speed. Furthermore, it might be fruitful to study closely the Fano factors of polyatomic molecules for protons and α particles, for the diversity of energy transfer processes is greater because of vibrational and rotational degrees of freedom in addition to the translation of a molecule as a whole.

The appreciable difference of the Fano factor for different particles is in sharp contrast with the W value, which is insensitive to different particles, as already noted by Platzman [1]. However, I find it mildly puzzling how to reconcile the close correlation [49, 51] of F and W with the observations of Doke and co-workers.

2.3. Outlook

The data surveys [9, 10] indicate that measured results are mostly for gases; in addition, semiconductors, e. g., silicon and germanium, have been studied for obvious interest as particle detector materials. From the point of view of basic physics, measurements on a wider range of materials will be stimulating.

I am unaware of any measurements on the statistical fluctuations in the number of excited states rather than ions. The simplest index of the fluctuations is the variance, and the ratio of the variance to the mean may be called the Fano factor for the yield of excited states. This quantity can be theoretically treated similarly as the Fano factor for ionization yield. More precisely, one should talk about a particular excited state, which may be detected and scored for instance through fluorescence, i. e., light emitted at a specific frequency, or through products of a specific chemical reaction. The cross section for discrete excitation by collisions of an electron or another charged particle shows different dependence on the kinetic energy, depending on the molecular species and on the character of a transition involved, for instance, whether it is dipole-allowed or not [7], while the ionization cross section shows generally similar dependence on the kinetic energy. Therefore, the Fano factor for the yield of excited states is a richer subject of study. Measurements of this kind may open up a new field of research.

3. I

3.1. Background

The I value I discuss here is different from the ionization threshold I that appeared in Sections 1 and 2. It is *the mean excitation energy* in the Bethe expression for the stopping power. For a particle of modest charge ze and sufficiently high speed $v = \beta c$, the stopping power, i. e., the mean energy loss per unit path length, in a medium with atomic number Z and sufficiently low atomic number density N is expressed as [7, 57]

$$S = (4\pi z^2 e^4/mv^2)\, NZ\, [\, \ln(2mv^2/I) - \ln(1 - \beta^2) - \beta^2]\, . \tag{8}$$

The mean excitation energy I is the sole nontrivial property of the stopping medium, and is defined in terms of the dipole oscillator-strength spectrum df/dE as [7, 57]

$$\ln I = \int \ln E\,(df/dE)\, dE\, /\, \int (df/dE)\, dE,. \tag{9}$$

where both of the integrals run over the entire range of excitation energies E including discrete and continuous. Most often the spectrum is normalized so that the denominator equals Z. Sometimes, for instance, in Fano [57], the denominator is set at unity. For a medium consisting of molecules, Z means the average atomic number as readily evaluated from the molecular structure, and N means the molecular number density.

For condensed matter, it is customary to express the oscillator-strength spectrum in terms of the dielectric-response function $\varepsilon(E)$, which represents the electric displacement induced by an applied electric field that has unit magnitude, is uniform in space, and oscillates at frequency $E/\hbar$. .The probability for the transfer of energy E from a fast charged particle to matter through glancing collisions is proportional to $\eta(E) = \mathrm{Im}\,[-1/\varepsilon(E)]$, and the product $E\,\eta(E)$ may be viewed as equal to df/dE, apart from a constant of proportionality [57]. This quantity is normalized as

$$\int E\,\eta(E)\, dE = (\pi/2)\, E_p^2, \tag{10}$$

where

$$E_p = \hbar\, (4\pi n_e\, e^2/m)^{1/2} \tag{11}$$

is the (nominal) plasma energy associated with the total electron density n_e. For a material of mass density d consisting of N molecules per unit volume that have mass A measured in atomic mass units and the total number of molecular electrons Z, one may evaluate E_p as

$$E_p = 28.816 \, (Zd/A)^{1/2} \, eV. \tag{12}$$

The I value thus defined plays a key role in the determination of stopping power. Unlike the ionization threshold, the mean excitation energy for stopping power is governed by the entire oscillator-strength spectrum, and is roughly proportional to Z; a rough estimate is given by $I/Z \approx 10$ eV, except for Z less than 10, for which I is larger that given by the relation. A more accurate estimate is often desirable because the stopping power is often amenable to measurements to a high precision; in general, when the stopping power is known under the condition of applicability of Eq. (8) to a precision of $\Delta S/S$, then it implies the knowledge of I to a precision of about 10 $\Delta I/I$. From the point of view of basic physics, the I value is linked with many other electronic properties through sum rules [7, 57] for the oscillator-strength spectrum, and is influenced by atomic aggregation and chemical binding, again as Platzman [58] pointed out many years ago.

3.2. Recent Developments

Data on stopping powers of various materials in general and on the I values in particular are reviewed in ICRU Report No. 37 [59] and No. 49 [60], and more recently in Chapter 7 of the IAEA Report [10]. What follows is discussion of a few key points.

For illustration of studies on the I value, we may begin with metallic aluminum, for which Shiles et al. [61] carried out a thorough analysis of the dielectric-response function. Figure 9 shows the evaluation of the I value. Notice the dominant contributions of the (nominally) eight electrons in the L shell, and the substantial contributions of the two electrons in the K shell, compared to the modest contributions of the three valence electrons chiefly responsible for the metallic binding. Table 1 shows

numerical values selected from different sources [17, 59, 61-64]. The theoretical value for metallic aluminum is consistent with the values derived from stopping-power measurements. It is markedly higher than the theoretical value for the free atom, chiefly owing to the shift of the valence-electron oscillator strengths at a few eV to the plasma energy around 15 eV. The same trends are seen in selected values for solid silicon [17, 59, 62, 65], shown in Table 2.

Another example concerns data on water [59, 66-70], shown in Table 3. The Bragg additivity of atomic contributions, as explained for instance in ICRU Report No. 37 [59], leads to 65 eV. The *I* values for water vapor from theory and experiment are in good agreement, and higher than the Bragg-additivity value. The *I* values for liquid water are even higher. The recent theoretical value agrees closely with the recent experimental value.

3.3. Outlook

In 1950 Platzman [58] stressed the importance of the complete oscillator-strength spectra as a basis for understanding radiation effects. When I started working with him in 1963, he expressed his hope for seeing extensive data over the far ultraviolet and soft x-ray regions, in which the bulk of the oscillator strength should lie, in view of the synchrotron radiation sources that began to be used at a few laboratories such as National Bureau of Standards and the Institute of Nuclear Study of the University of Tokyo. Now his hope has been realized to a large extent; measurements of the oscillator-strength spectra of many materials have been made at many synchrotron-radiation facilities, and related theoretical knowledge has been advanced, as seen for instance in Chapter 5 of the IAEA Report [10] and in the two-volume Handbook edited by Palik [71]. It will be fruitful to use the recent spectral data to evaluate the *I* values of many materials.

Finally, it is worthwhile to point out a deficiency in our current theoretical knowledge. The framework of our standard treatment of the oscillator-strength

spectrum, leading to standard sum rules and other general properties, rests on the dipole interaction and the nonrelativistic theory, and may be adequate for materials of modest atomic numbers, say, Z less than about 20. For materials consisting of higher-Z atoms, effects of higher multipole interactions and relativistic motions of atomic electrons need to be considered for high excitation energies at which an appreciable oscillator strength lies. In addition, corrections for relativistic motion of atomic electrons to the Bethe theory are beginning to be studied [72, 73]. The advent of measurements using high-energy photons point to ample opportunities for new and fruitful theoretical developments in this topic

Acknowledgments

References

[1] R. L. Platzman, Int. J. Appl. Radiat. Isot. 10 (1961) 116.

[2] R. L. Platzman, Radiat. Res. 2 (1955) 1.

[3] R. H. Fowler, Proc. Cambridge Phil. Soc. 21 (1923) 531.

[4] L. V. Spencer and U. Fano, Phys. Rev. 93 (1954) 1172.

[5] A. M. Weinberg and E. P. Wigner, The Physical Theory of Neutron Chain Reactors, (The University of Chicago Press, Chicago, 1958).

[6] P. G. Burke, in Atomic, Molecular, & Optical Physics Handbook, edited by G. W. F. Drake, (American Institute of Physics, Woodbury, New York, 1996), Chapter 45, p. 536.

[7] M. Inokuti, Rev. Mod. Phys. 43 (1971) 297.

[8] M. Inokuti, D. A. Douthat, and A. R. P. Rau, Phys. Rev. A 22 (1980) 445.

[9] International Commission on Radiation Units and Measurements, Average Energy Required to Form an Ion Pair, ICRU Report No. 31, (International Commission on Radiation Units and Measurements, Washington, D. C., 1979).

[10] International Atomic Energy Agency, Atomic and Molecular Data for Radiotherapy and Radiation Research. Final Report of a Co-ordinated Research Programme, Report No. IAEA-TECDOC-799, (International Atomic Energy Agency, Vienna, 1995).

[11] M. Kimura, M. Inokuti, and M. A. Dillon, in Advances in Chemical Physics, Vol. 84, edited by I. Prigogine and S. A. Rice, (John Wiley & Sons, New York, 1993), p. 193.

[12] M. Inokuti, K. Kowari, and M. Kimura, Phys. Rev. A 45 (1992) 4499.

[13] A. R. P. Rau, M. Inokuti, and D. A. Douthat, Phys. Rev. A 18 (1978) 971.

[14] M. Inokuti, J. L. Dehmer, and R. P. Saxon, in Argonne National Laboratory Radiological and Environmental Research Division Annual Report, July 1973 through June 1974. Report No. 75-3, Part I, p. 16.

[15] U. Fano, Phys. Rev. 70 (1946) 44.

[16] M. Inokuti, Radiat. Res. 64 (1975) 6.

[17] J. L. Dehmer, M. Inokuti, and R. P. Saxon, Phys. Rev. A 12 (1975) 102.

[18] W. P. Jesse, J. Chem. Phys. 55 (1971) 3603.

[19] D. Srdoc, B. Obelic, and I. Krajcar Bronic, J. Phys. B 20 (1987) 4473.

[20] M. Kimura, K. Kowari, M. Inokuti, I. Krajcar Bronic, D. Srdoc, and B. Obelic, Radiat. Res. 125 (1991) 237.

[21] R. L. Platzman, Radiat. Res. 17 (1962) 419.

[22] Y. Hatano, in Dynamics of Excited Molecules, edited by K. Kuchitsu, (Elsevier Science B. V., Amsterdam, 1994), p. 151.

[23] Y. Hatano, Interaction of Vacuum Ultraviolet Photons with Molecules -- Formation and Dissociation Dynamics of Superexcited States, to appear in Phys. Rept.

[24] E. Eggarter, J. Chem. Phys. 84 (1986) 6123.

[25] M. Inokuti and E. Eggarter, J. Chem. Phys. 86 (1987) 3870.

[26] M. Kimura and M. Inokuti, J. Chem. Phys. 87 (1987) 3875.

[27] M. Kimura, I. Krajcar-Bronic, M. Dillon, and M. Inokuti, Phys. Rev. A 45 (1992) 7831.

[28] M. Inokuti, M. Kimura, and M. A. Dillon, Phys. Rev. A 38 (1988) 1217.

[29] M. A. Dillon, M. Inokuti, and M. Kimura, Radiat. Phys. Chem. 32 (1988) 43.

[30] K. Kowari, M. Inokuti, and M. Kimura, Phys. Rev. A 42 (1990) 795.

[31] A. Pagnamenta, M. Kimura, M. Inokuti, and K. Kowari, J. Chem. Phys. 89 (1988) 6220.

[32] K. Kowari, M. Kimura, and M. Inokuti, J. Chem. Phys. 89 (1988) 7229.

[33] M. Inokuti, M. Kimura, and M. A. Dillon, Radiat. Phys. Chem. 34 (1989) 477.

[34] M. Kimura, M. Inokuti, K. Kowari, M. A. Dillon, and A. Pagnamenta, Radiat. Phys. Chem. 34 (1989) 481.

[35] M. A. Ishii, M. Kimura, M. Inokuti, and K. Kowari, J. Chem. Phys. 90 (1989) 3081.

[36] M. A. Ishii, M. Kimura, and M. Inokuti, Phys. Rev. A 42 (1990) 6486.

[37] M. A. Ishii, M. Kimura, and M. Inokuti, Phys. Rev. A 45 (1992) 190.

[38] K. Kowari and B. Shizgal, Chem. Phys. Lett. 176 (1991).

[39] K. Kowari and B. Shizgal, Appl. Radiat. Isot. 42 (1991) 985.

[40] K. Kowari and B. Shizgal, Chem. Phys. 185 (1994) 1.

[41] I. Krajcar-Bronic, M. Kimura, and M. Inokuti, J. Chem. Phys. 102 (1995) 6552.

[42] I. Krajcar-Bronic and M. Kimura, J. Chem. Phys. 103 (1995) 7104.

[43] K. Kowari, Phys. Rev. A 53 (1996) 853.

[44] K. Kowari and B. Shizgal, Chem. Phys. Lett. 260 (1996) 365.

[45] K. Kowari, K. Leung, and B. Shizgal, J. Chem. Phys. 108 (1998) 1587.

[46] R. D. Birkhoff, in Penetration of Charged Particles in Matter: A Symposium, (National Academy of Sciences, Washington, D. C. 1970), p. 1.

[47] R. H. Ritchie, C. J. Tung, V. E. Anderson, and J. C. Ashley, Radiat. Res. 64 (1975) 181.

[48] U. Fano, Phys. Rev. 72 (1947) 26.

[49] I. Krajcar Bronic, W Values and Fano Factors for Electrons in Rare Gases and Rare Gas Mixtures, to appear in Hoshasen (Ionizing Radiation).

[50] J. H. Hardy, A Course of Pure Mathematics, 10th Edition, (Cambridge University Press, Cambridge, 1952), p. 244.

[51] I. Krajcar Bronic, J. Phys. B 25 (1992) L215.

[52] T. Doke, N. Ishida, and M. Kase, Nucl. Instrum. Methods B 63 (1992) 373.

[53] M. Kase, T. Akioka, H.. Mamyoda, J. Kikuchi, and T. Doke, Nucl. Instrum. Methods 227 (1984) 311.

[54] N. Ishida, J. Kikuchi, and T. Doke, Jpn. J. Appl. Phys. 31 (1992) 1465.

[55] N. Ishida, J. Kikuchi, T. Doke, and M. Kase, Phys. Rev. A 46 (1992) 1676.

[56] J. Lindhard and V. Nielsen, Phys. Lett. 2 (1962) 209.

[57] U. Fano, Ann. Rev. Nucl. Sci. 13 (1963) 1.

[58] R. L. Platzman, in Symposium on Radiobiology. The Basic Aspects of Radiation Effects on Living Systems, Oberlin College, June 14-18, 1950, edited by J. J. Nickson, (John Wiley & Sons, New York, 1952), p. 139.

[59] International Commission on Radiation Units and Measurements, Stopping Powers for Electrons and Positrons. ICRU Report No. 37, (International Commission on Radiation Units and Measurements, Bethesda, MD, 1984).

[60] International Commission on Radiation Units and Measurements, Stopping Powers and Ranges for Protons and Alpha Particles. ICRU Report No. 49, (International Commission on Radiation Units and Measurements, Bethesda, MD, 1993).

[61] E. Shiles, T. Sasaki, M. Inokuti, and D. Y. Smith, Phys. Rev. B 22 (1980) 1612.

[62] C. Tschalär and H. Bichsel, Phys. Rev. 175 (1968) 476.

[63] N. Sakamoto, N. Shiomi-Tsuda, H. Ogawa, and R. Ishiwari, Nucl. Instrum. Methods B 33 (1988) 158.

[64] N. Sakamoto, H. Ogawa, M. Mannami, K. Kimura, Y. Suzuki, M. Hasegawa, I. Katayama, T. Noro, and H. Ikegami, Radiat. Eff. Def. Solids 117 (1991) 193.

[65] H. Bichsel, Rev. Mod. Phys. 60 (1986) 663.

[66] P. Dalton and J. E. Turner, Health Phys. 15 (1968) 257.

[67] G. D. Zeiss, W. J. Meath, J. C. F. MacDonald, D. J. Dawson, Radiat. Res. 70 (1977) 284.

[68] R. H. Ritchie, R. N. Hamm, J. E. Turner, and H. A. Right, in Sixth Symposium on Microdosimetry, Brussels, Belgium, May 22-26, 1978, edited by J. Booz and H. G. Ebert, (Harwood Academic Publishers, Ltd., London, 1978), p. 345.

[69] H. Bichsel and T. Hiraoka, Nucl. Instrum. Methods B 86 (1992) 345.

[70] M. Dingfelder, D. Hantke, M. Inokuti, and H. G. Paretzke, Radiat. Phys. Chem. 53 (1998) 1.

[71] E. D. Palik (ed.), Handbook of Optical Constants of Solids, (Academic Press, Orlando, 1985); Volume 2, (Academic Press, Boston, 1991).

[72] P. T. Leung, M. L. Rustgi, and S. A. T. Long, Phys. Rev. A 33 (1986) 2827.

[73] P. T. Leung, Phys. Rev. A 40 (1989) 5417.

Tables

Table 1. The mean excitation energy I for stopping power of aluminum

Source, Year	Basis of determination	Value
Tschalär and Bichsel, 1968 [62]	Stopping power for protons, 3 - 30 MeV	167 eV
Dehmer et al., 1975 [17]	From theoretical df/dE for a free atom	124 eV
Shiles et al., 1980 [61]	From $\eta(E)$ of metallic aluminum	\165.7 eV
ICRU No. 37, 1984 [59]	Recommendation	166 eV
Sakamoto et al., 1988 [63]	Stopping power for 6.5-MeV protons	169.7 eV
Sakamoto et al., 1991 [64]	Stopping power for 73-MeV protons	169.4 eV

Table 2. The mean excitation energy I for stopping power of silicon

Source, Year	Basis of determination	Value
Tschalär and Bichsel, 1968 [62]	Stopping power for protons, 3 - 30 MeV	173 eV
Dehmer et al., 1975 [17]	From theoretical df/dE for a free atom	131 eV
ICRU No. 37, 1984 [59]	Recommendation	173 eV
Bichsel, 1986 [65]	From $\eta(E)$ of silicon solid	174 eV

Table 3. The mean excitation energy I for stopping power of water

Source, Year	Basis of determination	Value
	Bragg additivity	65 eV
Dalton and Turner, 1968 [66]	Stopping power of vapor	71.3 eV
Zeiss et al., 1977 [67]	From df/dE of vapor	71.6 eV
Ritchie et al. 1978 [68]	From $\eta(E)$ of liquid	75 eV
ICRU No. 37, 1984 [59]	Recommendation for vapor	71.6 eV
	Recommendation for liquid	75.0 eV
Bichsel and Hiraoka, 1992 [69]	Stopping power of liquid for protons of 30 - 70 MeV	79.8 eV
Dingfelder et al., 1998 [70]	From $\eta(E)$ of liquid	81.8 eV

Captions for Figures

Fig. 1. The yield spectrum, i. e., the integrand of Eq. (3), for the mean N_i of the number of ion pairs produced in molecular hydrogen at 1 atm under incidence of an electron of kinetic energy of 10 keV (reproduced with permission from Inokuti et al. [8]). The degradation spectrum is here expressed as $y(T_0, T)$, which means $y(T)$ resulting specifically from a single source electron of kinetic energy T_0. The ordinate quantity contains the factor $1/T_0$ for convenience.

Fig. 2. The W values of atomic vapors as a function of the atomic number Z, taken from Inokuti et al. [14]. The solid line represents W_a, viz., the W value for high-energy electrons evaluated by using the approximate method of Inokuti [16]. The broken line represents W_F, viz., the W value evaluated by using the approximate method of Fano [15]. The squares show more accurate theoretical results, and the circles experimental results, for comparison.

Fig. 3. The ratio W/I of atomic vapors as a function of the atomic number Z, taken from Inokuti et al. [14]. The solid line represents W_a/I, where W_a is the W value for high-energy electrons evaluated by using the approximate method of Inokuti [16]. The broken line represents W_F/I, where W_F is evaluated by using the approximate method of Fano [15]. The squares show more accurate theoretical results, and the circles experimental results, for comparison.

Fig. 4. The W value for linear alkanes as a function of the number of carbon atoms, reproduced with permission from Kimura et al. [20]. The open circles represent theoretical results of Kimura et al. [20] for 1.5 keV electrons. The triangles represent experimental results for 1.5-keV electrons [19]. The filled circles, connected by dashed

curves represent the values for high-energy electrons recommended in ICRU Report No. 31 [9].

Fig. 5. The yield spectrum, i. e., the second integrand of Eq. (4), for the variance V_i of the number of ion pairs in molecular hydrogen at 1 atm under incidence of an electron of kinetic energy of 10 keV, shown by the broken curve. The solid line represents the yield spectrum for the mean, as given in Fig. 1, and is included here for comparison. The degradation spectrum is here expressed as $y(T_0, T)$, which means $y(T)$ resulting specifically from a single source electron of kinetic energy T_0. The ordinate quantity contains the factor $1/T_0$ for convenience. (This figure is reproduced with permission from Inokuti et al. [8].)

Fig. 6. The ratio $\rho_i(T)/\sigma_i(T)$ as a function of electron kinetic energy T, where $\rho_i(T)$ is the quantity defined by Eq. (5), and $\sigma_i(T)$ is the total ionization cross section for molecular hydrogen. (This figure is reproduced with permission from Inokuti et al. [8].)

Fig. 7. The Krajcar Bronic relation between F and W/I. The filled squares represent rare gases, the open circles molecular gases, the diamonds Ar-H_2 mixtures, and the filled triangles mixtures exhibiting the metastable Penning effect. (Courtesy: I. Krajcar Bronic. This figure has been taken from Krajcar Bronic [49].)

Fig. 8. The relation between F and W for Ar-H_2 mixtures at varying compositions (Courtesy: I. Krajcar Bronic. This figure has been taken from Krajcar Bronic [49].)

Fig. 9. The mean excitation energy for stopping power of metallic aluminum (reproduced with permission from Shiles et al. [61]). The vertical axis represents the mean excitation energy $I(E_m)$ with respect to the spectrum truncated at energy E_m, and the horizontal

axis the energy E_m of truncation. In other words, $I(E_m)$ was evaluated from Eq. (9) in which the two integrals are taken from zero to E_m.
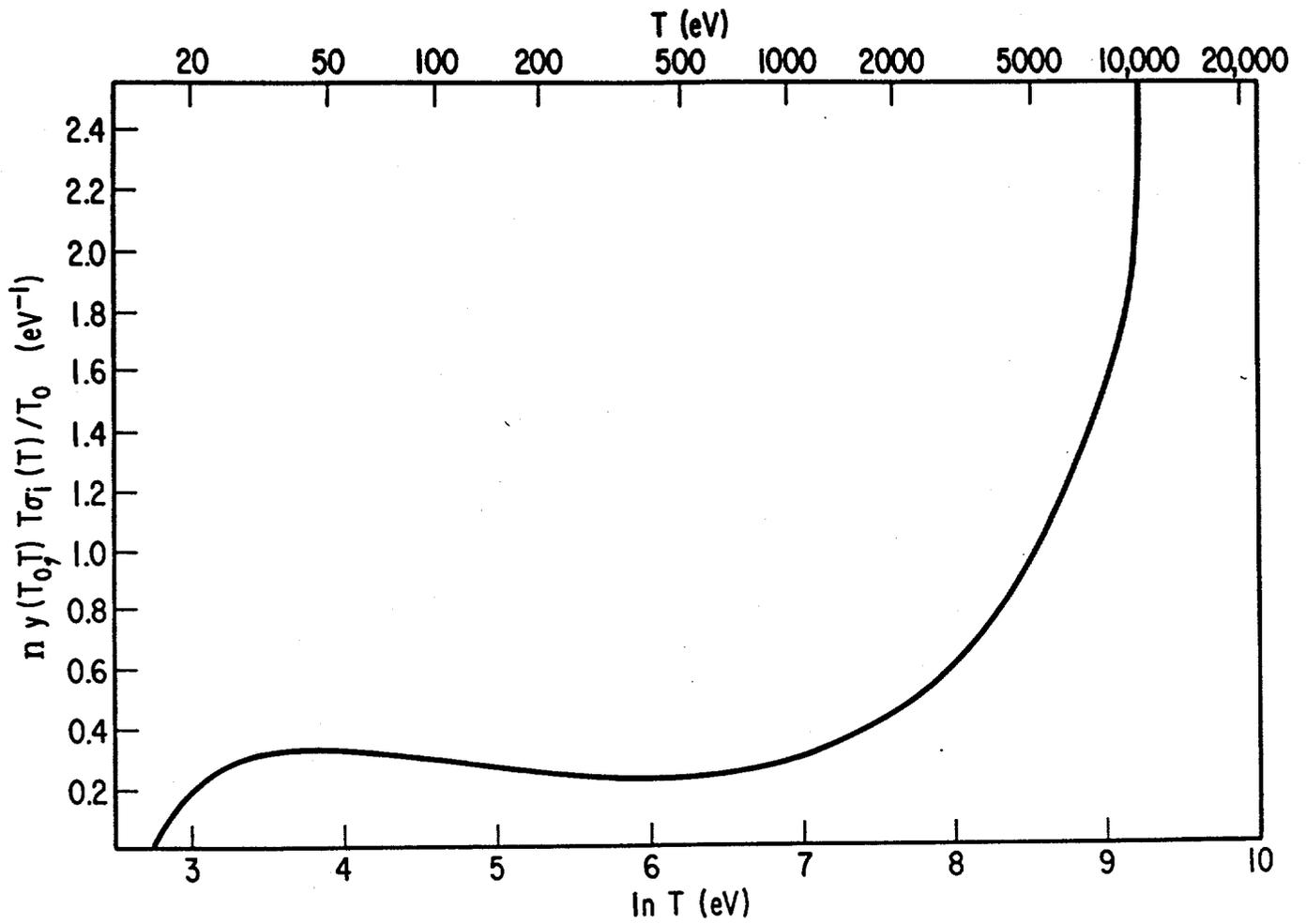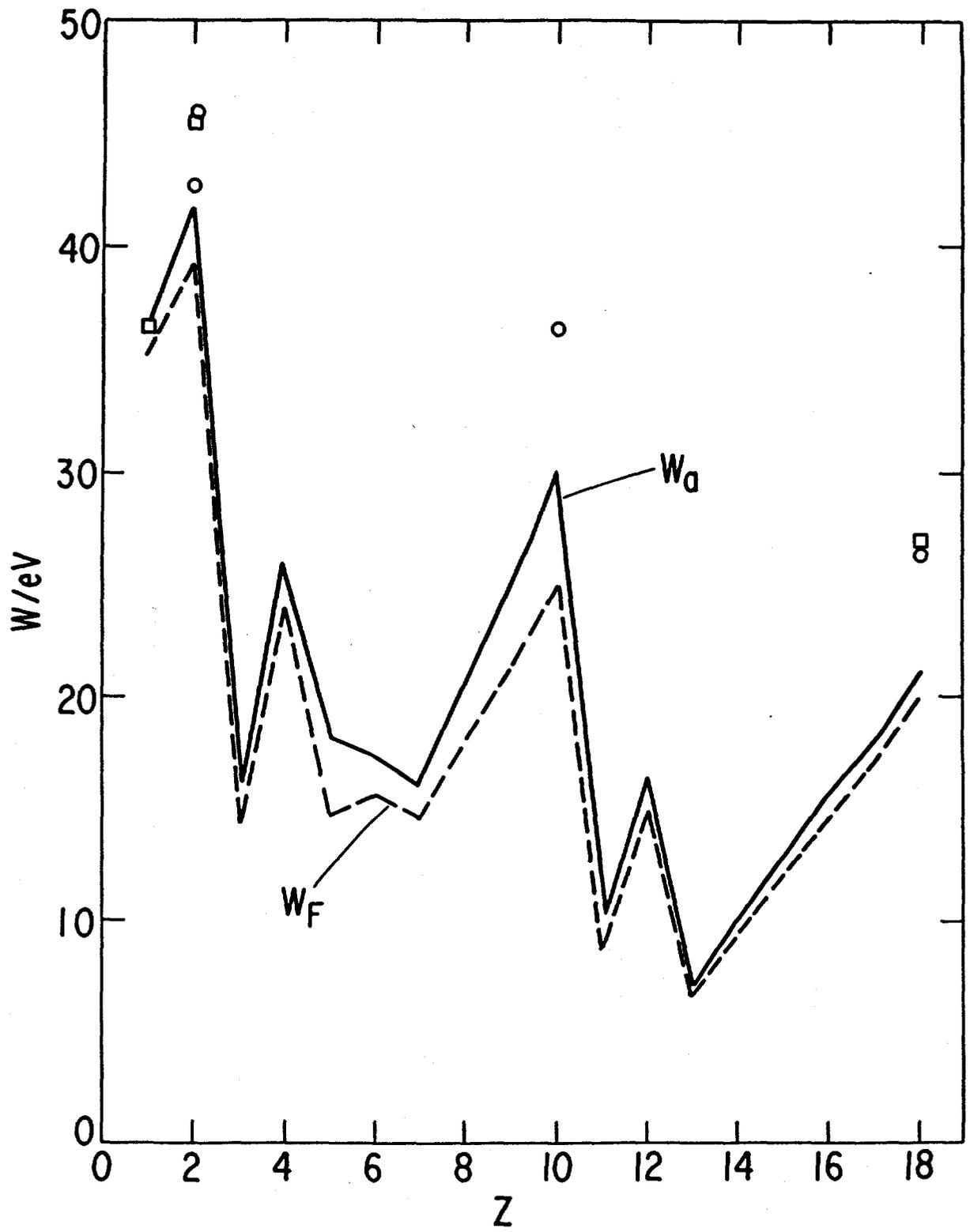
Fig. 1 of M. Inokuti
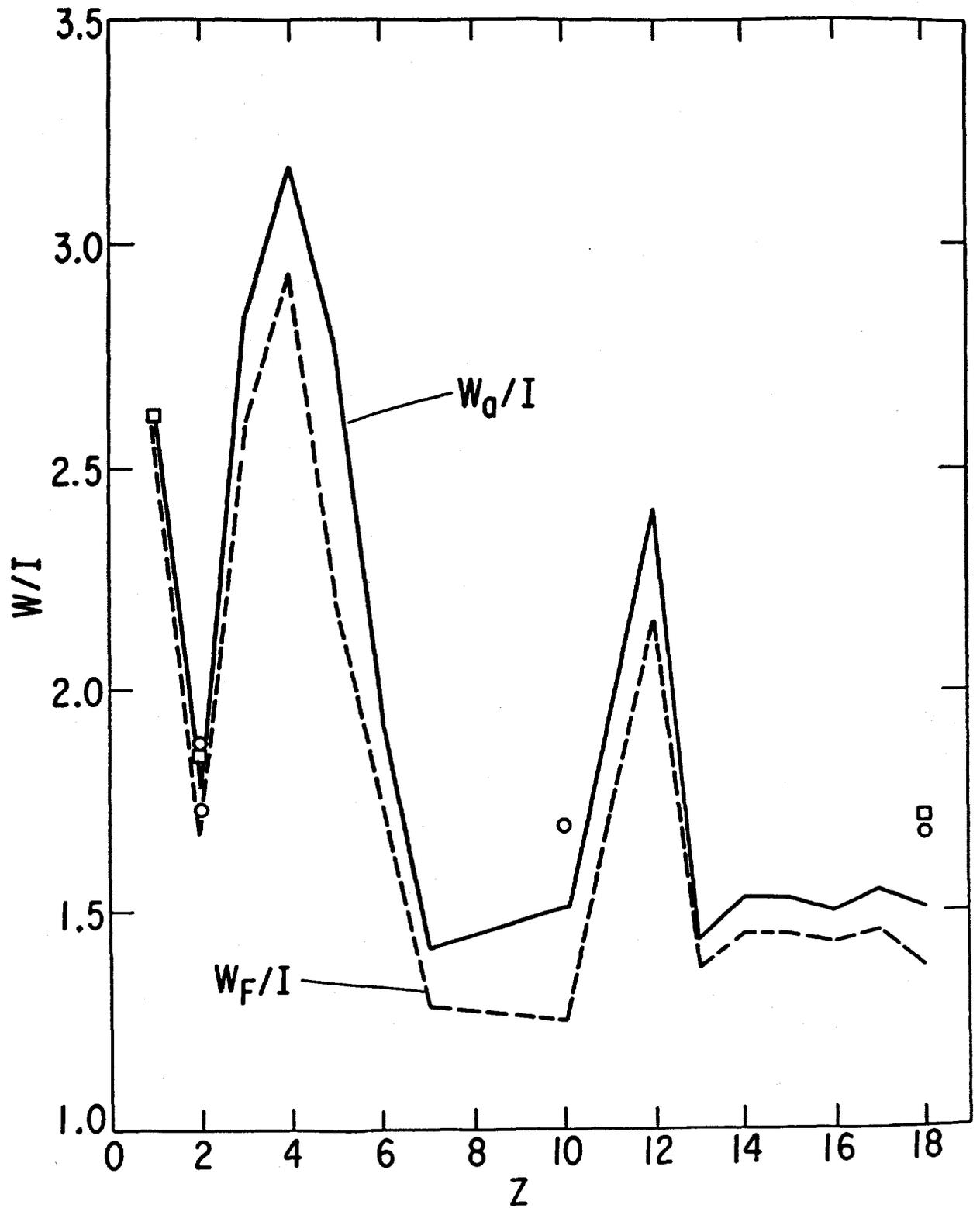
Fig. 2 of M. Inokuti

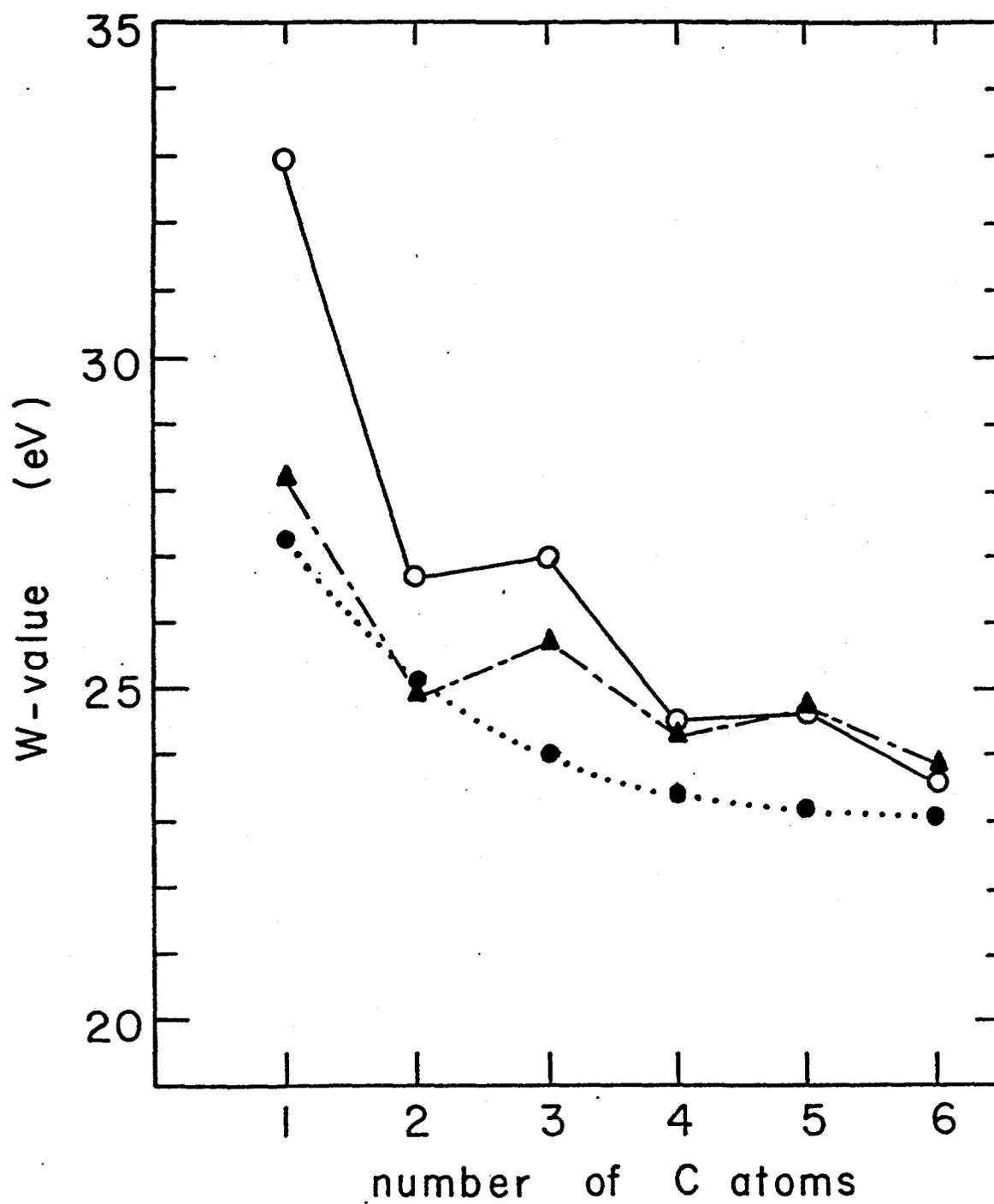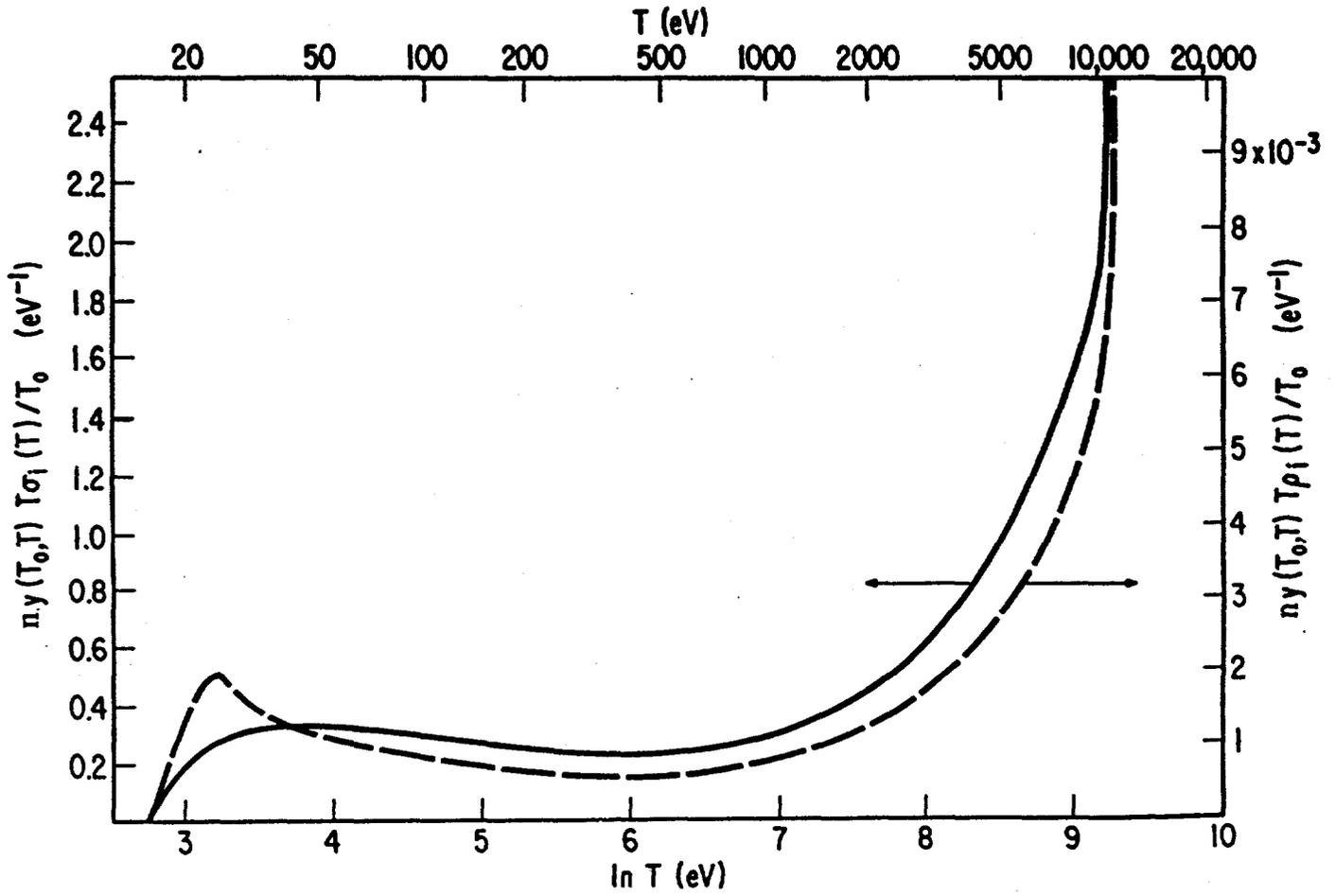Fig. 3 of M. Inokuti

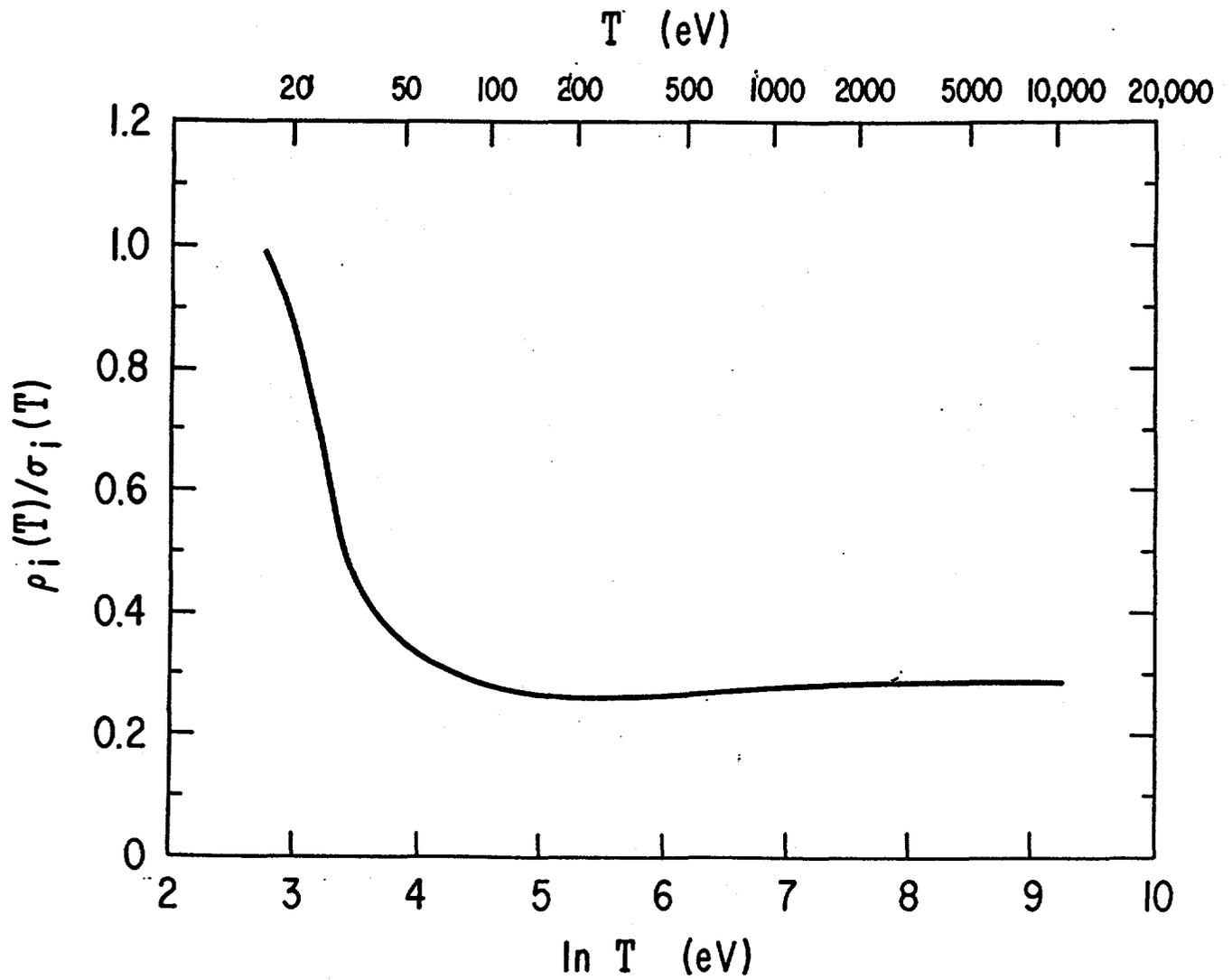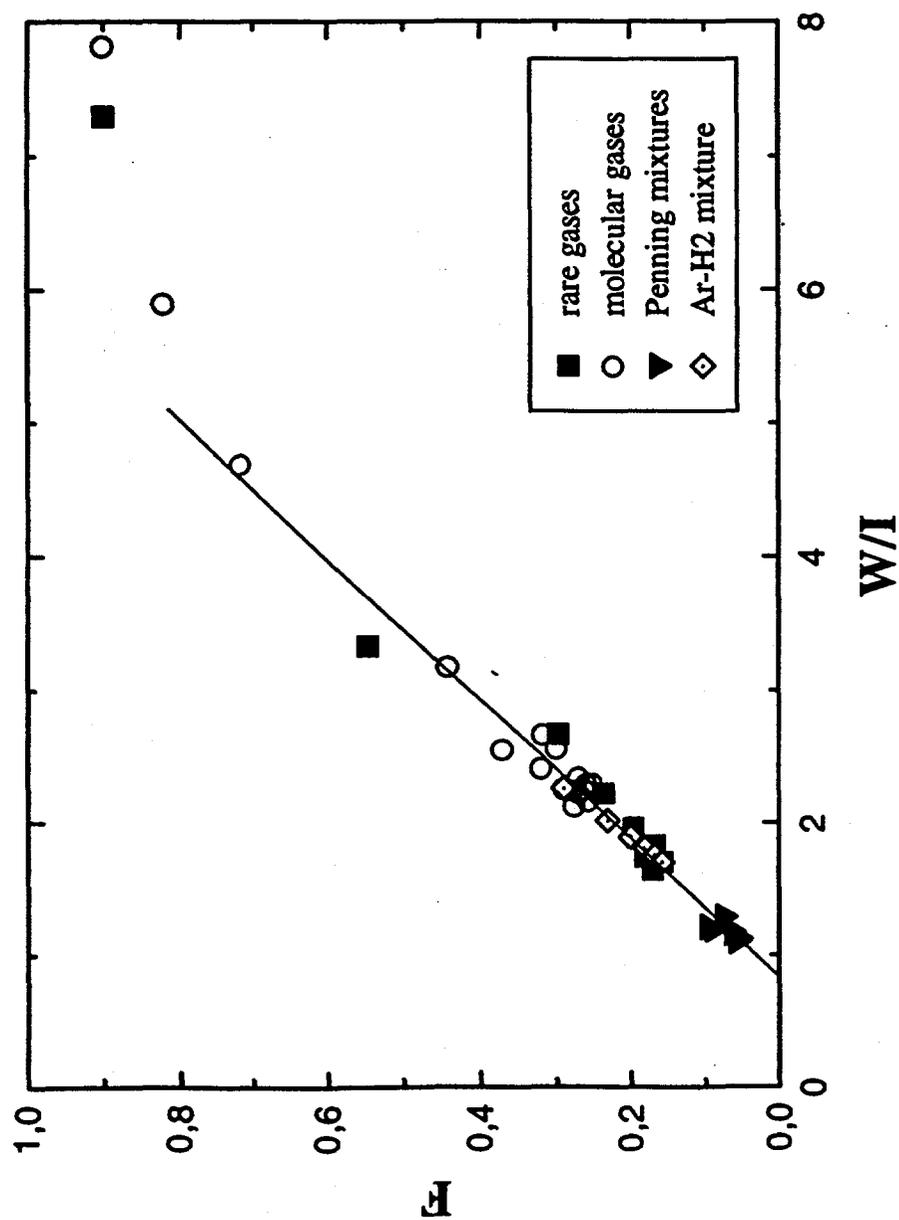Fig. 4 of M. Inokuti

Fig. 5 of M. Inokuti
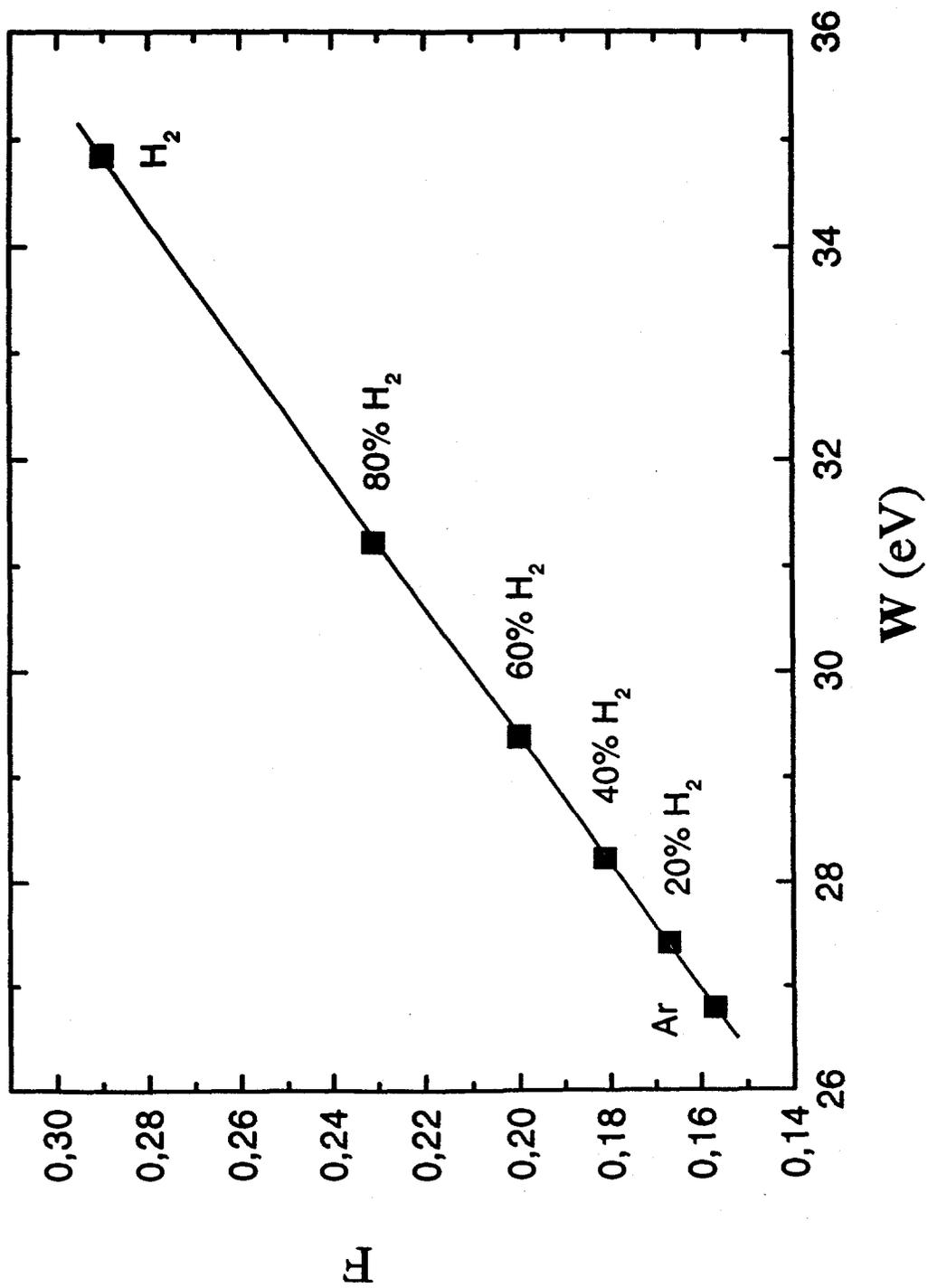
Fig. 6 of M. Inokuti

Fig. 7 of M. Inokuti

Fig. 8 of M. Inokuti

Fig. 9 of M. Inokuti

Fig. 9 of M. Inokuti