THRESPECT – A PROGRAM FOR THE DETERMINATION OF THE APPEARANCE ENERGIES OF NEUTRAL AND IONIZED SPECIES

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Abstract. Collisions of photons and charged particles with molecules lead to their excitation, ionization, and dissociation into neutral and ionized fragments. Accurately determining thresholds of the formation of particular products plays a vital role in analyzing processes occurring during these interactions. Therefore, we present a computer program, "ThreSpect," that allows calculating threshold energies of various species generated in these collisions irrespective of whether they are recorded with mass spectrometric or emission spectroscopic techniques.

Key words: appearance threshold, Wannier threshold law, ThreSpect program, optimization, excitation, ionization, dissociation.

1. INTRODUCTION

Electromagnetic radiation and charged particles found in space or applied in medicine and engineering affect matter at the macroscopic and microscopic scales. The most severe modifications are produced at the molecular level, where radiation often triggers compounds' excitation, ionization, and fragmentation. These processes produce electrons, chemically active ions, excited molecules, and reactive free radicals. Each molecule has well-defined ionization and bond energies, so a precisely defined energy value specifies when a given product should appear. This minimal energy is associated with a particular interaction mechanism.

Therefore, to identify how physicochemical reactions proceed at the molecular level, it is necessary to determine the threshold energies (ionization/appearance energies, E_A) of respective products as accurately as possible. It can be performed experimentally by measuring particular product cross-section changes as a function of incident electron/ion/photon energy. Then, the usual way of determining E_A is to fit an appropriate theoretical threshold law to these results.

Two methods have been used routinely to determine the E_A. The first one is a cross-curve approximation. In this approach, experimental results are interpolated to

two crossed curves, one fitted to the background points and one to the points at a rising slope using the least-squares method. Then, the energy value is determined at the point of intersection of these lines [1]. This method is vague because it does not consider the energy dispersion of the radiation beam, *i.e.*, the finite energy resolution of the electrons/ions/photons incident on the target. The calculated threshold energy values are also higher than the real ones. The second method considers the beam's energy dispersion by convolution of the Wannier threshold law and Gaussian function, representing the energy dispersion distribution implemented in the standard data analysis and graphing software (see, *e.g.* [2–6]). This approach is also vulnerable to malfunction because the researchers' subjective eyeball assessment determines the curve fit.

A theoretical E_A closest to the real value can only be obtained by programming these mathematical functions and performing a fully automatic fitting process utilizing iterative non-linear optimization algorithms. However, no commercial or free software is dedicated to determining the threshold energies to our knowledge. Therefore, we present a proprietary computer program, "ThreSpect," addressing this gap. Our approach involves programming the convolution of Gaussian and Wannier functions and employing the Trust-Region-Reflective Least Squares algorithm [7] to solve the curve-fitting problem. The program's functionality and examples of determining the threshold energies of some species known from the scientific literature are presented.

2. THRESPECT SOFTWARE DESCRIPTION

2.1. THRESHOLD LAW MODEL

The ionization or dissociation process requires depositing a well-defined portion of energy in the atom or molecule. The ionization energy represents the lowest energy required to remove an electron from an atomic or molecular system. The appearance energy of the specific fragmentation product is the minimum energy required to induce a reaction, usually involving the excitation or ionization of the molecule followed by fragmentation. Below these values, the processes do not occur. The probability of these processes changes with a rise in the energy of the incident radiation above these minimal values, usually increasing the corresponding cross-section in the near-threshold region. Wannier's threshold law [8] is widely employed to simulate a small energy region close to the expected value of the threshold energies (ionization or appearance energies, E_A). This semi-classical theoretical model was used initially for the impact of electrons on atoms and ions [8] but has recently been employed to analyze many species generated by utilizing different spectroscopic techniques (see, *e.g.* [2–6, 9–13]). In particular, a comprehensive characterization of the Wannier model and its advantages and disadvantages related to electron-induced ionization and fragmentation of noble gases and CH_4 were presented in the [10] and [13] papers, respectively.

Let us assume that a Wannier-type function, $w(E)$, can be written as follows:

$$w(E) = \begin{cases} (aE + b);\ E < E_A \\ (aE + b) + \sigma_W (E - E_A)^n;\ E \geq E_A \end{cases} \quad (1)$$

where E is the incident impact energy, and a, b, σ_W, and n are the adjustable parameters. Note that $(aE + b)$ represents the fitting to the gradually rising background signal. The (1) function does not consider the energy dispersion of the radiation beam. This energy distribution of the beam can be described by the Gaussian function, $g(E)$ [6]:

$$g(E) = \frac{1}{\sigma_G \sqrt{2\pi}}\, e^{-\frac{(E-\mu)^2}{2\sigma_G^2}}\ , \quad (2)$$

where σ_G corresponds to the standard deviation of the incident beam and μ is the energy of the center of its peak. The convolution of the Gaussian function (equation (2)) with the standard Wannier function (equation (1)) produces a modified Wannier function ($w*g$) that expresses how the shape of $w(E)$ is modified by the $g(E)$ radiation beam energy distribution:

$$(w * g)(E) = \int_{E_A}^{\infty} \left[\frac{1}{\sigma_G \sqrt{2\pi}} e^{-\frac{(E_x-\mu)^2}{2\sigma_G^2}} \right] [(aE_x + b) + \sigma_W (E_x - E_A)^n]\, dE_x\ . \quad (3)$$

Here, the σ_G parameter is related to the full width at half maximum (FWHM) of the peak according to the relation:

$$FWHM = 2\sqrt{2 \ln 2}\, \sigma_G = 2.3548 \cdot \sigma_G\ . \quad (4)$$

Expression (3) allows determining threshold energies E_A and n-Wannier exponents of various products from the fittings to the measured cross-section curves, no matter whether the species were generated from collisions with electrons, ions, or photons and detected with mass spectrometric or emission spectroscopic techniques. Our model also considers the rising background and the radiation beam's energy dispersion. A similar method implemented in the standard data graphing software to the electron impact ionization of the gas phase furanose alcohols was recently suggested [12] to be more accurate than simple Wannier functions. We expect a fully automatic fitting process to give an even better agreement with the actual E_A values.

2.2. PROGRAM FUNCTIONALITY

The "ThreSpect" software was written in the "Python" version 3.8.3 code language. Python was used because it has many well-resourced libraries. The following

Python libraries were implemented in the program: tkinter, matplotlib, sys, webbrowser, numpy, lmfit, and date-time. From the libraries, scipy.integrate packages were used. These packages provide easy-to-use and straightforward tools enabling the construction of fitting models for non-linear least-squares problems that can be applied to real data [14]. The program uses Least-Squares minimization – the Trust Region Reflective method [15], to determine the best-fit curve using the least-squares method for curvilinear functions.

The program works correctly if the data set is adequately prepared. The program reads experimental data only from text files with a ".txt" extension. Data in the ".txt" file must consist of two columns separated by at least one space. The columns must not contain titles. By default, the program considers the first column as the *x*-axis coordinates and the second one as the *y*-axis coordinates. A dot separates decimal numbers.

After starting the program, the file explorer should be used to select the file for analysis. When loading the file, the range of values of the *x*-axis should be defined. The FWHM value of the spectrometer's electron/ion/photon beam should be entered in the next step. At this stage, one can also set the initial values of other parameters. Almost every cross-section experimental curve has some background that can be approximated by fitting a straight line. The software enables the determination of the parameters *a* and *b* of such a line in two ways. In the first mode, we can determine them through a separate module that allows the line to fit the selected background points using the least-squares method. The *a* and *b* coefficients may also be set as constant in the primary fitting procedure. In the second mode, the program performs the curve fitting procedure to the experimental points, and the primary function can determine the *a* and *b* coefficients apart from other parameters. The program automatically saves all the parameters of the fitted curve in the file called "auto save.txt." This file is created automatically in the folder in which the program is located. After each run of the functions, the program will add new data below the previous ones. One can also save data in a file *via* the file explorer in a text file and a graph in the extensions ".png."

We performed several simulations, which showed that the best starting point to obtain reasonable results is to free all parameters. Note that the procedure allows for individual parameters to be kept fixed. The program finds a solution, even if it starts far from the absolute minimum. However, to ensure the simulation runs correctly, one should implement a set of initial parameters as close as possible to the expected values.

In Fig. 1, we present the output data of the example simulation. The first line contains the date and time of the simulation. This information allows us to distinguish between different program runs. The file's analyzed name is printed in the following line. After a fitting method has been completed successfully, fitted variables, standard errors for the fitted variables, and correlations between pairs of fitted variables are automatically calculated from the covariance matrix [14]. The results of these calculations are given in the following lines, apart from the values of fitted variables.

The program lists the following coefficient values with their uncertainties in absolute and relative terms: n – Wannier exponent, sigma_Wannier – σ_W, sigma_Gauss – σ_G, E – threshold energy (E_A), and μ, a, b. Note that sigma_Gauss corresponds to the standard deviation of the incident beam, which is automatically set by the program when the FWHM value is entered. The value μ refers to the actual energy of the incident electron beam of the Gaussian function. Below these results, energies and simulated (Intensity (sim)) and experimental (Intensity (exp)) intensities of the near-threshold cross-section curve are finally given.

```
Date 2022-05-20 and time 16:55:29
_____argon 21.txt_____ 2022-05-20 16:55:29
**********************************************
[[Fit Statistics]]
   # fitting method   = least_squares
   # function evals   = 144
   # data points      = 31
   # variables        = 7
   chi-square         = 1.5121e+09
   reduced chi-square = 63005919.2
   Akaike info crit   = 562.786982
   Bayesian info crit = 572.824892
[[Variables]]
   n:            1.38586880 +/- 1.16686696 (84.20%) (init = 1)
   sigma_Wannier:  2407106.56 +/- 1276137.21 (53.02%) (init = 500)
   sigma_Gauss:    0.39406474 +/- 0.07721165 (19.59%) (init = 0.2547965)
   E:            15.9244341 +/- 0.18201674 (1.14%) (init = 13.5452)
   mi:           16.4141238 +/- 0.49085968 (2.99%) (init = 13.5452)
   a:            54.4825898 +/- 2014872.06 (3698194.36%) (init = 0)
   b:            902739.074 +/- 33406084.9 (3700.52%) (init = 0)
[[Correlations]] (unreported correlations are < 0.100)
   C(a, b)                      = -0.999
   C(n, mi)                     = -0.990
   C(sigma_Wannier, b)          =  0.974
   C(sigma_Wannier, a)          = -0.971
   C(sigma_Gauss, E)            =  0.832
   C(n, E)                      = -0.763
   C(sigma_Wannier, mi)         =  0.755
   C(n, sigma_Gauss)            = -0.740
   C(n, sigma_Wannier)          = -0.736
   C(E, mi)                     =  0.718
   C(mi, b)                     =  0.712
   C(mi, a)                     = -0.689
   C(sigma_Gauss, mi)           =  0.671
   C(n, b)                      = -0.664
   C(n, a)                      =  0.639
   C(sigma_Wannier, E)          =  0.197
   C(sigma_Wannier, sigma_Gauss) =  0.182
**********************************************
_____Curve coordinates_____
Energy     Intensity (sim)      Intensity (exp)
13.80000 1.4784822e-05      2.8800000e+03
```

Fig. 1 – The output data of the example simulation performed using ThreSpect.

3. EXAMPLES OF APPLICATION

Threshold energies were *in silico* generated and compared to experimental spectra of many products measured using different experimental techniques to test the accuracy of predictions. Illustrative examples of our program applications using the fit procedure described above to a few cross-sections are only presented. Figure 2 shows the cross-section curves (open circles) and the corresponding fits (solid lines) for three cations and two fragment neutrals. Table 1 lists the threshold energies, E_A, of the corresponding products investigated. The spectroscopic values or the results from original works [3, 9, 10, 16, 17] are also presented for comparison.

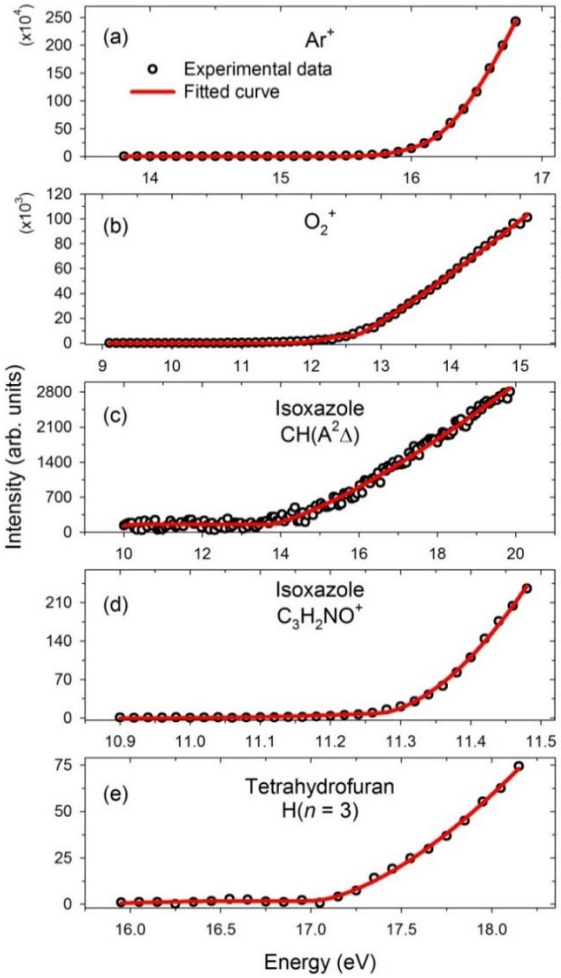

Fig. 2 – The cross-section curves measured using different experimental techniques in narrow energy regions near the expected thresholds. The solid lines represent the best fit to the experimental data (circles).

Table 1

Threshold energies, E_A, in eV for the formation of different products compared with other spectroscopic appearance energies, E_{ASpec}. The designations in the first column link the corresponding panels in Fig. 2. EIMS – electron impact mass spectrometry, EIFS – electron impact fluorescence spectroscopy, PIMS – photon-induced mass spectrometry, and PIFS – photon-induced fluorescence spectroscopy

No.	Product/technique	E_A [eV] this work	n this work	E_{ASpec} [eV]
(a)	Ar^+/ EIMS	15.9 (0.2)	1.4 (1.2)	15.76 (0.01) [10]
(b)	O_2^+/ EIMS	12.29 (0.09)	1.17 (0.03)	12.0696 (0.0003) [16]
(c)	$CH(A^2\Delta)$ / EIFS	13.71 (0.13)	1.31 (0.05)	14.00 (0.40) [17]
(d)	$C_3H_2NO^+$/ PIMS	11.27 (0.02)	1.50 (0.50)	11.19 (0.05) [3]
(e)	H(n = 3) / PIFS	17.00 (0.07)	1.58 (0.11)	17.00 (0.10) [9]

At first, it was checked how the program works for electron-induced ionization energy determinations of atoms and small molecules. The cross-sections for production of the Ar^+ (Fig. 2, panel (a)) and O_2^+ (Fig. 2, panel (b)) as a function of incident electron energy were measured for purposes of the present work using an EPIC 300 (Hiden Analytical Ltd.) quadrupole mass spectrometer (EIMS technique). The description of this apparatus and its operational modes is out of this article's scope; thus, we refer the reader to, *e.g.*, [18] for more information.

All the parameters were set free during the fittings to Ar^+ (see Fig. 1). As seen in Fig. 2 (a), the fitting curve and the Ar^+ cross-sections are in excellent agreement. The obtained E_A is 0.14 eV higher than the most accurate value of the appearance energy of Ar^+ (15.76 (0.01) eV) [10]. In this case, our n exponent is higher than the result obtained by Gstir *et al.* (1.27 (0.05) eV) [10] and the generalized Wannier prediction of 1.127 [8] (see Table 1). Since the Wannier exponent corresponds to the curvature of the function in the near-threshold region, its lower values may be obtained when almost zero-kinetic-energy electrons are used in the experiment. However, the present experimental results are inherently influenced by the energy resolution of the electron spectrometer used, which may enhance the value of the n exponent [19].

Similar simulations were performed for electron-induced dissociative ionization of simple and more complex molecules. The energy shift in Ar^+ between the E_A and the spectroscopic value of the ionization energy (15.76 (0.01) eV [10]) was further used to calibrate the energy scale in each such measurement using the electron impact mass spectrometry (EIMS) technique. As an example, the simulation of the O_2^+ cross-section is only shown here. The fitting and the O_2^+ data shown in Fig. 2 (b) indicate good agreement. The determined energy threshold for O_2^+ production reasonably agrees with the spectroscopic ionization energy from [16]. Note that the n-Wannier exponent is consistent with theoretical predictions [8].

Since the ThreSpect program worked well in determining E_A of ionization energies measured by electron impact mass spectrometry, we applied it to the determination of neutral and ionic fragments measured using different spectroscopic

techniques, *i.e.*, electron impact fluorescence spectroscopy [17], photon-induced mass spectrometry [3], and photon-induced fluorescence spectroscopy [9].

Figure 2 (c) presents the emission cross-section of the $CH(A^2\Delta)$ fragment measured in electron-induced neutral fragmentation of isoxazole [17]. The points are somewhat scattered compared to the experimental data shown in (a) and (b) panels. However, the fitting extensively reproduces the general trend. The original work [17] obtained the E_A from a cross-curve approximation. As seen in Table 1 present result is 0.29 eV lower than the original value. Such a difference was expected, given the discussion presented above.

We also tested our program in a situation where threshold energies were previously determined using an implementation of equation (3) in the standard data analysis and graphing software. Figures 2 (d) and (e) show examples of ThreSpect simulations to the experimental data taken from [3, 9]. As seen in Figures 2 (d) and (e) and Table 1 the present results are in excellent agreement with the previous ones.

4. SUMMARY AND OUTLOOK

Computer simulations of naturally occurring phenomena gain much attention and find widespread applications. In particular, simulation techniques help study complex systems effectively, especially where applying analytical methods would be demanding or even impossible. One such problem is implementing a minimization procedure in non-linear least-squares curve fitting dedicated to determining the threshold energies. Accurately determining thresholds for creating different products is essential in investigating mechanisms occurring during radiation interactions with matter, whether they are probed by mass spectrometry or emission spectroscopy techniques.

Here, we presented a computer program, "ThreSpect," enabling a fully automatic fitting procedure utilizing iterative non-linear optimization algorithms. By employing this program, we have simulated various curves measured by us using the EIMS technique and determined previously using different spectroscopic techniques. The program's functionality and only a few examples of determining the threshold energies are presented here. The fittings allowed for a reliable statistical analysis of accumulated counts and gave good agreement between E_A obtained by us with values from other studies.

Nevertheless, the simulations showed some drawbacks. The most important one was the information that a small energy step and large signal-to-noise ratio should characterize the data subjected to analysis to achieve a reliable statistical analysis. The program can fit data in unfavorable conditions (*e.g.*, a few experimental points, significant energy steps, and a low number of counts above background) but does not calculate correlations between the determined parameters. During the

analysis, we additionally recognized that some cross-section curves could contain more thresholds due to another process leading to the product with the same m/q ratio or an additional ionic state (see, *e.g.*, total ion yield obtained in the dissociative photoionization of isoxazole molecules [3], or cross-section curves in [13]). Therefore, we would like to implement the possibility of the fitting procedure simulating higher thresholds in the future.

The computer program supporting this study's findings is freely available in the Gdansk University of Technology Bridge of Knowledge repository [20].

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