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Extracting Cross Sections from Rate Coefficients: Application to Molecular Gas Dissociation

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The deconvolution of temperature-dependent rate coefficients to energy-dependent cross sections is accomplished by using a nonlinear optimization technique. The suggested method is successfully applied to atom–molecule and molecule–molecule dissociation processes in hydrogen.

Nomenclature

E = collision energy, J
$\boldsymbol{e}$ = unit vector
F = least mean-square measure of distance between two rate coefficients, cm^6 s^{-2}
$k(T)$ = rate coefficient, cm^3 s^{-1}
K_B = Boltzmann constant, JK^{-1}
m_r = reduced mass, kg
N_T = number of temperature points considered in minimization process
$\boldsymbol{P}$ = vector of independent variables parametrizing a given functional form for a cross section
T = temperature, K
σ = cross section, Å^2

I. Introduction

LARGE interest is presently being devoted to the development of state-to-state kinetics for evaluating the dissociation and ionization degrees of diatomic molecules under nonequilibrium conditions typically met in plasma and aerospace applications [1]. In these studies, the coupling of dissociation/recombination kinetics to nonequilibrium vibrational kinetics is very often of paramount importance. A consistent coupling can be realized by solving a set of coupled rate equations (CREs). Another widespread approach is to solve the set of coupled Boltzmann transport equations for the gas mixture via a Monte Carlo method (direct simulation Monte Carlo (DSMC) [2,3]). The latter approach is particularly useful when rarefaction effects or strong gradients (e.g., in strong shocks) cause strong nonequilibrium deviations in the particle velocity distribution functions. In this case, any modeling of the relaxation kinetics based on continuum fluid dynamics becomes inaccurate. As is well known, the DSMC method needs energy-dependent cross sections $\sigma(E)$ as input instead of the temperature-dependent rate coefficients $K(T)$ used in the CRE approach. Cross sections and rate coefficients are linked for a two-body collision by the well-known relation [4]

$$k(T) = (\pi m_r)^{-(1/2)}(2/K_B T)^{3/2} \int_0^\infty \sigma(E) E e^{-(E/K_B T)}\, \mathrm{d}E \tag{1}$$

the expression being valid for a Maxwellian velocity distribution function. It would be desirable that molecular dynamics studies provide both cross-sectional and rate coefficient data on the same footing. However, the evaluation of a single rate coefficient requires the knowledge of the cross section in a number of points that is roughly proportional to the number of temperature values required. This number is, normally, much smaller than the number of energy values required for a satisfactory evaluation of the corresponding cross section. In the rate coefficient calculation, in fact, the cross section is weighted by a Maxwellian distribution. This averaging procedure also makes the evaluation of rate coefficients more robust with respect to the accuracy required in the evaluation of the corresponding cross section. As a consequence, cross-sectional data for collision between heavy particles (either from theoretical calculations or from experiments) are far more scattered than corresponding rate coefficient data.

It would therefore be desirable to have a means of inverting Eq. (1) in order to derive cross sections from the knowledge of the corresponding rate coefficients. Numerical techniques for the Laplace inversion exist and have been used in the past [5–7], but since this is mathematically an ill-posed problem, they are prone to introduce unphysical features in the calculated cross sections. From the knowledge of the rate coefficient in a sufficiently large temperature range, it is still possible, however, to extract the cross section by imposing some constraint on its functional form.

Accuracy requirements, in this approach, are only imposed in a weak sense, i.e., by setting limits to the distance (in this work, defined by the F measure) between the original and the reconstructed rate coefficients. This weak convergence criterion does not exclude that mathematical solutions of the inverse Laplace transform problem [Eq. (1)] present strong oscillations or other nonphysical features [8]. Previous attempts [9] have been successful, but they have also shown that this success depends strongly on the range and accuracy of available input data.

We propose to use a nonlinear optimization technique to invert Eq. (1) with a suitably parameterized cross section. Control on the physical properties of the results can then be achieved by choosing the proper functional form suited to the process under study.

To validate the method, cross sections obtained from molecular dynamics calculations are integrated to give reference rate

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coefficients. The rate coefficients are then input to a standard nonlinear optimization algorithm [downhill simplex method (DSM) [10]] to give reconstructed cross sections that satisfy the weak convergence criterion described previously. The cross sections thus obtained are then compared with the original data in order to assess the feasibility and reliability of the method.

This method of constrained optimization, from a mathematical point of view, is analogous to the maximum entropy method applied in other fields to the solution of ill-posed mathematical problems ([11] and references therein), the optimization criterion being the only difference.

Note that the inversion of Eq. (1) has been proposed by Bird [12] in order to obtain chemical reaction probabilities from rate coefficients. That method, however, is only applicable to an Arrhenius-like functional form for the rate coefficient. Furthermore, the functional form used for the reaction cross section (actually, the reaction probability) entails the estimation of macroscopic quantities, such as the average number of degrees of freedom.

The processes selected for this study are (vibrationally selected) impact dissociations in collisions with molecules and parent atoms. While DSM has found application to several optimization problems in physics and engineering, its application to the functional inverse Laplace transformation is considered here for the first time.

II. Computational Method

The functional inverse Laplace transformation is obtained by minimization of the least mean-square measure of distance F between the reference rate coefficient and the rate coefficient obtained from a properly parameterized test cross section.

Let $\sigma(E, \boldsymbol{P})$ be the test cross section, parameterized by the n-dimensional real vector $\boldsymbol{P}$; the value to be minimized by the optimization algorithm is then

$$F(\boldsymbol{P}) = \sum_{j=1}^{N_T} [k(T_j) - s(T_j, \boldsymbol{P})]^2 \tag{2}$$

$$s(T_j, \boldsymbol{P}) = (\pi m_r)^{-(1/2)} (2/K_B T_j)^{3/2} \int_0^\infty \sigma(E, \boldsymbol{P}) E e^{-(E/K_B T_j)} \, \mathrm{d}E \tag{3}$$

where $k(T_j)$ is the reference rate coefficient at temperature T_j, and N_T is the number of temperatures where $k(T_j)$ is known. The integral in Eq. (3) is evaluated numerically using the trapezoidal rule [13]. The energy range considered in the integration is about $10K_B T_{N_T}$, with T_{N_T} being the largest temperature value for which the reference rate coefficient is known. Choosing a lower limit for the temperature (e.g., $5K_B T_{N_T}$) reduces the possibility of correctly reconstructing the cross section at high energy, because the related information in the rate coefficient is lacking in that case. On the contrary, using a much higher energy limit (e.g., $20K_B T_{N_T}$) introduces spurious results, because the high energy part of the cross section (not contributing significantly to the rate) is left in an undecided state by the minimization procedure.

For the test cross section, we choose an empirical LeRoy class II functional form [14] to describe the threshold processes (as also suggested by Martin et al. [15]):

$$\sigma(E, \boldsymbol{P}) = x_1 \frac{(E - x_4)^{x_2}}{E} e^{-x_3(E - x_4)} \tag{4}$$

where $\boldsymbol{P} = (x_1, x_2, x_3, x_4)$, so that the minimization occurs in the four-dimensional space of P vectors.

The principle of the minimization algorithm is as follows. In an n-dimensional space, a simplex is defined as an n-dimensional figure specified by giving its $n + 1$ vertices. The algorithm is started by providing an initial guess for a simplex (five $\mathbf{P}$ vectors in our case) in the search space. The algorithm then makes its way downhill through an n-dimensional topography until it encounters, at least, a local minimum in the function to be optimized [function F in Eq. (2)]. In practice, only one vector, $\boldsymbol{P_0}$, is required, while the other n vectors can be obtained from

$$\boldsymbol{P}_i = \boldsymbol{P}_0 + \Delta \boldsymbol{e}_i \qquad i = 1, \ldots, 4 \tag{5}$$

where $\boldsymbol{e_i}$ are n linearly independent unit vectors, and Δ is a constant that is a guess of the problem's characteristic length scale. When the required accuracy is reached, the algorithm stops and outputs the $\tilde{\mathbf{P}}$ vector that minimizes the F function; the function $\tilde{\sigma} = \sigma(E, \tilde{\mathbf{P}})$ is therefore the extracted cross section.

Note that, at variance with other optimization techniques, the DSM method requires only function evaluations at $n + 1$ points, and not derivatives.

III. Results

The processes chosen for this study are the dissociation of the hydrogen molecule by impact with either hydrogen atoms or molecules. The first example is the dissociation by atom impact,

$$\mathrm{H} + \mathrm{H}_2(v, j = 0) \rightarrow 3\mathrm{H} \tag{6}$$

for selected values of the vibrational quantum number v.

Reference cross sections have been obtained from quasi-classical trajectory (QCT) calculations [16]. In these calculations, the hydrogen molecule is assumed to have 15 vibrational levels and a dissociation energy of 4.4772 eV. Table 1 reports corresponding rate coefficients obtained by Esposito and Capitelli [17] and Esposito et al. [18]. From these rate coefficients, cross sections are extracted by the inverse Laplace transformation described in Sec. II. They are compared with the original reference cross sections in Fig. 1. The agreement is very good in the whole energy range (0–9 eV in this case). Cross-sectional parameters obtained by DSM corresponding to Fig. 1 are reported in Table 2.

As a second test, consider collision-induced dissociation of $\mathrm{H}_2(v = 0, j = 0)$ in collision with $\mathrm{H}_2(v = 0, j = 0)$,

$$\mathrm{H}_2(v = 0, j = 0) + \mathrm{H}_2(v = 0, j = 0) \rightarrow \mathrm{H}_2 + 2\mathrm{H} \tag{7}$$

Table 1 Rate coefficients ($\mathrm{cm}^3\,\mathrm{s}^{-1}$) for selected dissociation processes [Eq. (6)] as obtained from QCT calculations

T, K	$v = 0$	$v = 5$	$v = 10$	$v = 14$
100	4.502E – 266	2.332E – 128	2.316E – 45	1.474E – 11
500	3.424E – 62	3.921E – 35	4.043E – 18	4.314E – 10
1,000	7.286E – 37	2.164E – 23	2.666E – 14	9.329E – 10
1,500	2.078E – 28	2.698E – 19	6.622E – 13	1.331E – 09
2,000	3.710E – 24	3.809E – 17	3.710E – 12	1.664E – 09
2,500	1.388E – 21	8.352E – 16	1.110E – 11	1.954E – 09
3,000	7.494E – 20	7.005E – 15	2.391E – 11	2.216E – 09
3,500	1.332E – 18	3.346E – 14	4.238E – 11	2.456E – 09
4,000	1.179E – 17	1.116E – 13	6.618E – 11	2.680E – 09
4,500	6.524E – 17	2.913E – 13	9.475E – 11	2.889E – 09
5,000	2.595E – 16	6.384E – 13	1.274E – 10	3.087E – 09
5,500	8.104E – 16	1.229E – 12	1.636E – 10	3.275E – 09
6,000	2.107E – 15	2.141E – 12	2.027E – 10	3.455E – 09
6,500	4.750E – 15	3.452E – 12	2.442E – 10	3.627E – 09
7,000	9.568E – 15	5.227E – 12	2.877E – 10	3.793E – 09
7,500	1.759E – 14	7.525E – 12	3.328E – 10	3.952E – 09
8,000	3.002E – 14	1.039E – 11	3.792E – 10	4.106E – 09
8,500	4.813E – 14	1.384E – 11	4.266E – 10	4.254E – 09
9,000	7.324E – 14	1.791E – 11	4.747E – 10	4.398E – 09
9,500	1.066E – 13	2.259E – 11	5.234E – 10	4.538E – 09
10,000	1.494E – 13	2.787E – 11	5.725E – 10	4.673E – 09
20,000	3.225E – 12	2.041E – 10	1.440E – 09	6.561E – 09
30,000	7.419E – 12	3.533E – 10	1.873E – 09	7.156E – 09
40,000	1.003E – 11	4.218E – 10	1.982E – 09	7.012E – 09
50,000	1.119E – 11	4.391E – 10	1.934E – 09	6.566E – 09
60,000	1.146E – 11	4.306E – 10	1.822E – 09	6.033E – 09
70,000	1.126E – 11	4.105E – 10	1.691E – 09	5.503E – 09
80,000	1.082E – 11	3.859E – 10	1.559E – 09	5.014E – 09
90,000	1.027E – 11	3.604E – 10	1.435E – 09	4.573E – 09
100,000	9.693E – 12	3.357E – 10	1.321E – 09	4.183E – 09

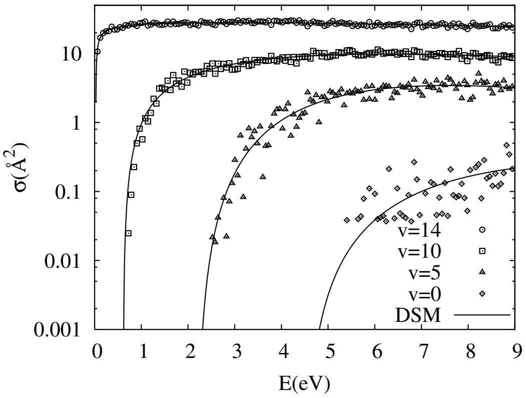

Fig. 1 Comparison between cross sections obtained by DSM (full lines) and by QCT (symbols).

Both rates and cross sections, for this process, have been reported by Martin et al. [15]. We use their temperature-dependent rate coefficients to obtain the corresponding DSM cross sections. Again, excellent agreement is found between calculated and original cross sections (Fig. 2). Table 3 reports the parameters for the calculated cross sections. Keeping the dynamical threshold energy parameter x_4 as a free adjustable parameter in the minimization procedure improves the efficiency and the performance of the method. Note that the physical threshold energy is very well reproduced by the calculated parameter.

As a last example, the method is applied to the low energy results of Ceballos et al. [19] for the reaction

$$H_2(v, j = 0) + H_2(w = 0, j = 0) \rightarrow H_2 + 2H \tag{8}$$

involving different vibrational levels, v. Again, both rates and cross sections have been obtained from QCT calculations.

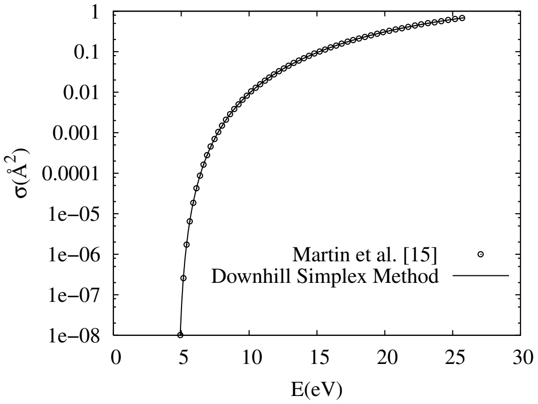

Fig. 2 Comparison between cross sections obtained by DSM and by Martin et al. [15] for the dissociation process [Eq. (7)].

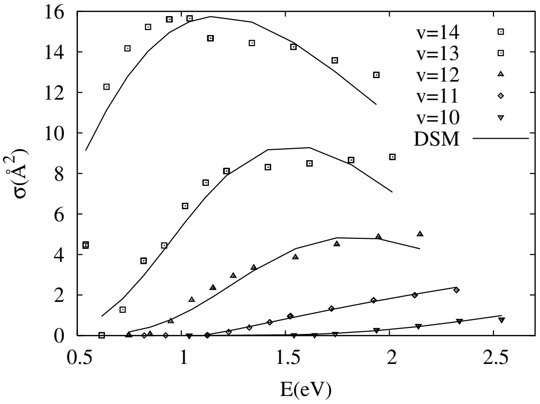

Fig. 3 Comparison between cross sections obtained by DSM (full lines) and by Ceballos et al. [19], Energy in collision is measured from threshold.

Table 2 Cross-sectional parameters obtained by DSM for Fig. 1

v	x_1	x_2	x_3	x_4
0	0.113	2.80	0.304	4.4772
5	1.50	3.13	0.448	2.185
10	6.20	1.89	0.175	0.615
14	28.4	1.12	4.58E − 02	2.42E − 2

Table 3 Cross-sectional parameters obtained by DSM for Fig. 2

Parameter	Value
x_1	5.59E − 05
x_2	4.70
x_3	7.94E − 02
x_4	4.70

Table 4 Cross-sectional parameters obtained by DSM for Fig. 3

Vibrational level	x_1	x_2	x_3	x_4
10	1.81	8.02	2.48	0.698
11	4.10	1.39	3.09E − 13	1.08
12	271	8.14	4.53	0.225
13	466	6.94	4.17	9.46E − 02
14	99.3	3.10	1.84	2.50E − 2

A comparison between calculated and QCT cross sections is shown in Fig. 3 (corresponding cross-sectional parameters are reported in Table 4), showing good agreement for each vibrational quantum number. In this case, due to the limited temperature range of the reference data, the energy range over which the calculated cross sections could be determined with some degree of confidence is also limited.

IV. Conclusions

A nonlinear optimization technique is used to extract cross-sectional data from temperature-dependent rate coefficients. The method has been tested on hydrogen dissociation processes for which both cross sections and rate coefficients are available. The method is simple to implement (DSM modules are freely available in the literature, e.g., the AMOEBA code in [13]). Requirements include the selection of a suitable functional form for the cross section, which must somehow be tailored to the process under consideration; in addition, the temperature range over which the reference rate coefficients are known must be compatible with the energy range over which the cross-sectional evaluation is required.

Results are encouraging and suggest its use with (experimentally or theoretically derived) rate coefficients where corresponding cross sections are not available.

Future plans concern the application of the method to molecule–molecule vibrational energy exchange processes. These are resonant or quasi-resonant processes (thus, very different from the impact dissociation studied here) for which cross-sectional data are very scarce, while tables of rate coefficients are available in the literature.

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