



# Electron-scattering cross sections for $\text{TiCl}_3$

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A consultancy project for **Tokyo Electron Technology Solutions Ltd.**



## Project Scope

The *ab initio* electron-scattering cross sections for  $\text{TiCl}_3$  will be computed using the R-matrix method. The following processes will be considered for cross section calculations.

- Elastic scattering
- Momentum transfer
- Electronic excitation
- Rotational excitation
- Neutral dissociation
- Dissociative electron attachment
- (Dissociative) ionization

## Executive summary

The summary of reactions studied in the present report is listed in Table I. The corresponding cross sections are provided in data files with the unit convention for energy in eV and cross sections in  $\text{\AA}^2$ .

TABLE I: Executive Summary

Process Type and energy range	Reaction
Elastic Scattering Momentum Transfer	$e^- + \text{TiCl}_3 \rightarrow e^- + \text{TiCl}_3$
Rotational Excitation	$e^- + \text{TiCl}_3(j = 0) \rightarrow e^- + \text{TiCl}_3(j = 1, \dots, 5)$
Electronic Excitation	$e^- + \text{TiCl}_3(X) \rightarrow e^- + \text{TiCl}_3(n = 1, 2, \dots, 6)$
Electron-impact Dissociation	$e^- + \text{TiCl}_3 \rightarrow e^- + \text{TiCl}_2 + \text{Cl}$
Dissociative Electron Attachment	$e^- + \text{TiCl}_3 \rightarrow \text{TiCl}_2 + \text{Cl}^-$
Electron-impact Ionization	$e^- + \text{TiCl}_3 \rightarrow \text{TiCl}_3^+ + 2e^-$

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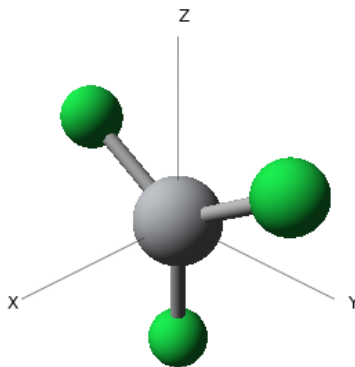


FIG. 1: Equilibrium geometry of  $\text{TiCl}_3$ .

## Literature Review

Figure 1 shows the equilibrium geometry of  $\text{TiCl}_3$  (CAS number 7705-07-9, Titanium trichloride) [1]. No cross sections for  $\text{TiCl}_3$  were found in the literature.

## Elastic scattering and momentum transfer

The total electron-impact elastic scattering and momentum transfer cross sections for  $\text{TiCl}_3$  are shown in Fig.2.

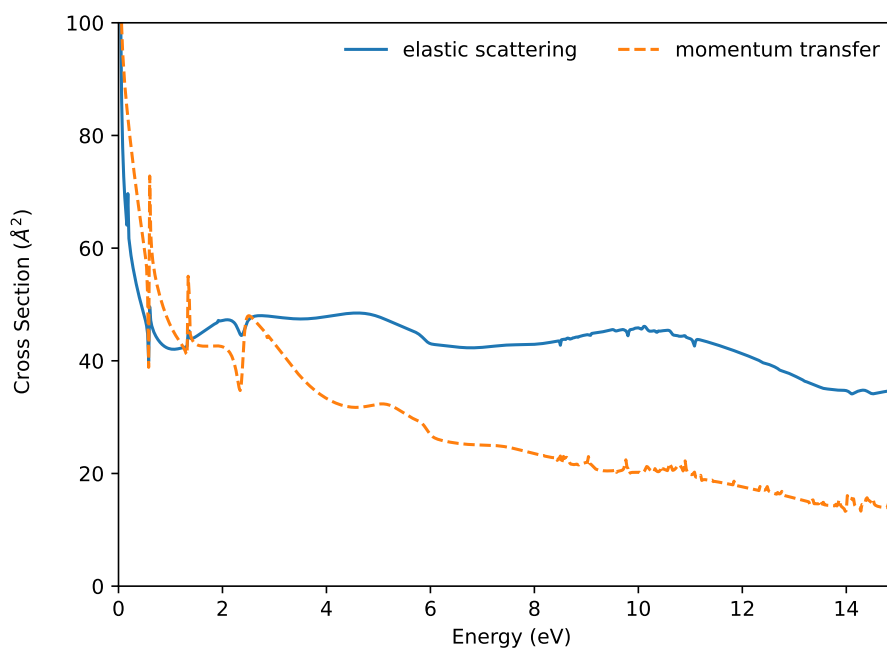


FIG. 2: Total elastic scattering and momentum transfer cross sections for  $\text{TiCl}_3$ .

## Electron-impact excitation

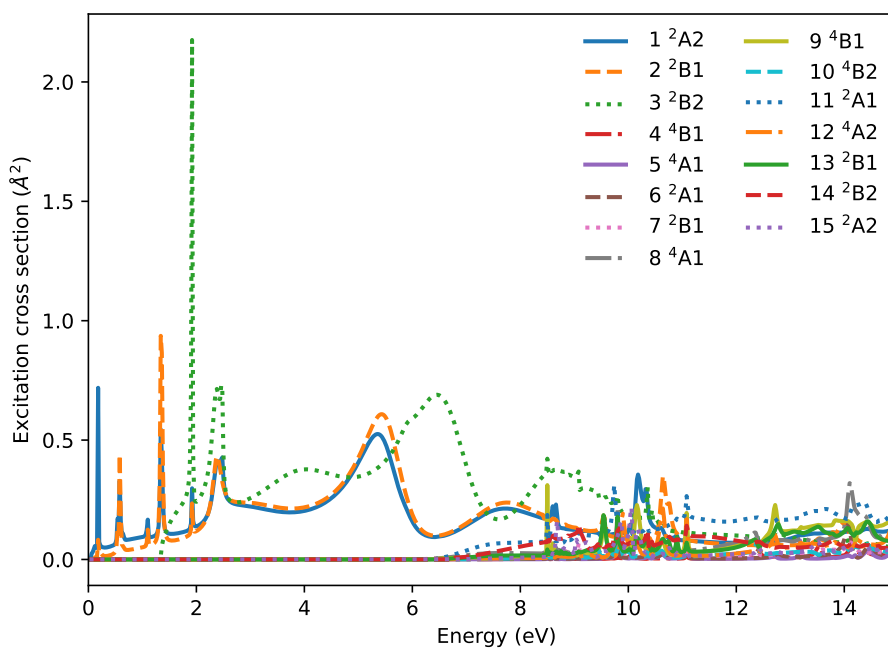
The electron-impact excitation cross sections for  $\text{TiCl}_3$  are shown in Fig.3. The vertical excitation energies for the excited levels are given in Table II.

State	VE (eV)
$X - {}^2A_1$	0
1 - ${}^2A_2$	0.05
2 - ${}^2B_1$	0.10
3 - ${}^2B_2$	1.33
4 - ${}^4B_1$	5.76
5 - ${}^4A_1$	5.93
6 - ${}^2A_1$	6.07
7 - ${}^2B_1$	6.13
8 - ${}^4A_1$	6.13
9 - ${}^4B_1$	6.28
10 - ${}^4B_2$	6.38
11 - ${}^2A_1$	6.44
12 - ${}^4A_2$	6.45
13 - ${}^2B_1$	6.66
14 - ${}^2B_2$	6.79
15 - ${}^2A_2$	6.86

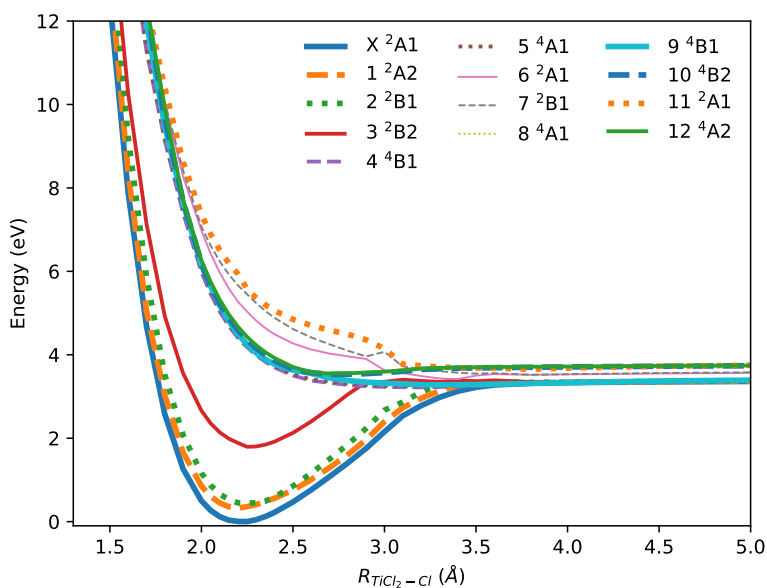
**TABLE II:** Calculated vertical excitation energies (VE) in eV for  $\text{TiCl}_3$  relative to the ground state.

## Neutral dissociation

To investigate neutral dissociation (via excitation), we first investigate the potential curves for  $\text{TiCl}_3$ . The potentials for the ground and excited states are shown in Fig.4 as a function of the Ti-Cl bond length. As a function of this bond length, most of the potentials are dissociative above their excitation thresholds, although the first three excited states could contain bound states. These states are only considered dissociative at energies above the dissociation threshold of 3.5 eV.

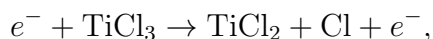


**FIG. 3:** Electron-impact excitation cross sections for the excited levels of  $\text{TiCl}_3$ .



**FIG. 4:** Potential energy curves for the excited levels of  $\text{TiCl}_3$  as a function of the  $\text{TiCl}_2\text{-Cl}$  bond length.

The dissociation cross section for the process



is shown in Fig.5, and is obtained by summing all of the excited-state cross sections at energies at which the respective states are considered to be dissociative.

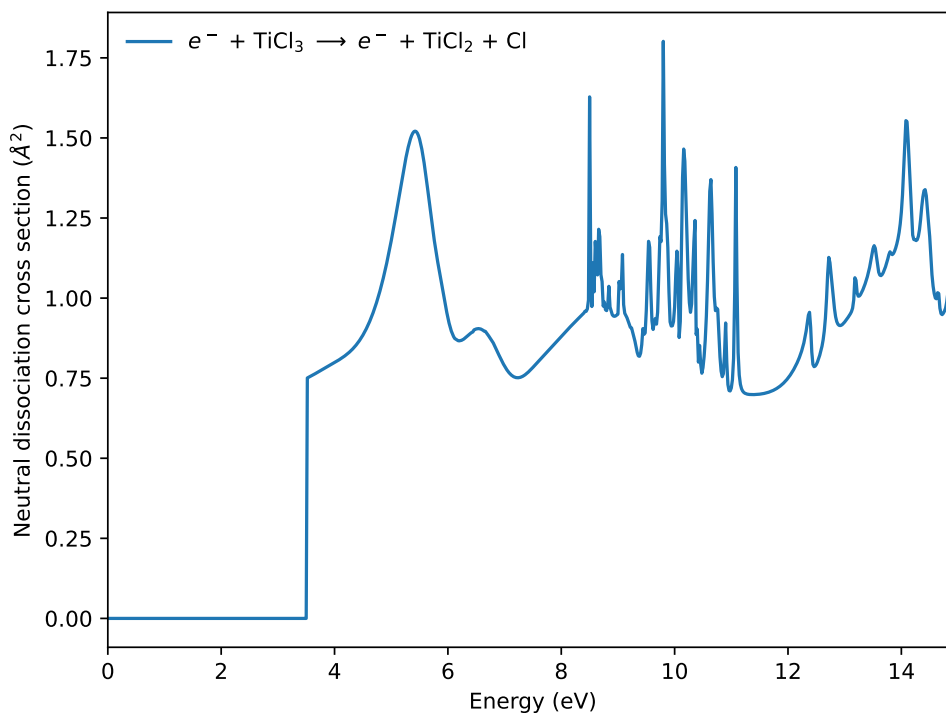


FIG. 5: Neutral dissociation cross section for TiCl<sub>3</sub>.

## Electron-impact rotational excitation

The electron-impact rotational excitation cross sections for TiCl<sub>3</sub> for  $j = 0$  to  $j' = 1, \dots, 5$  are shown in Fig.6.

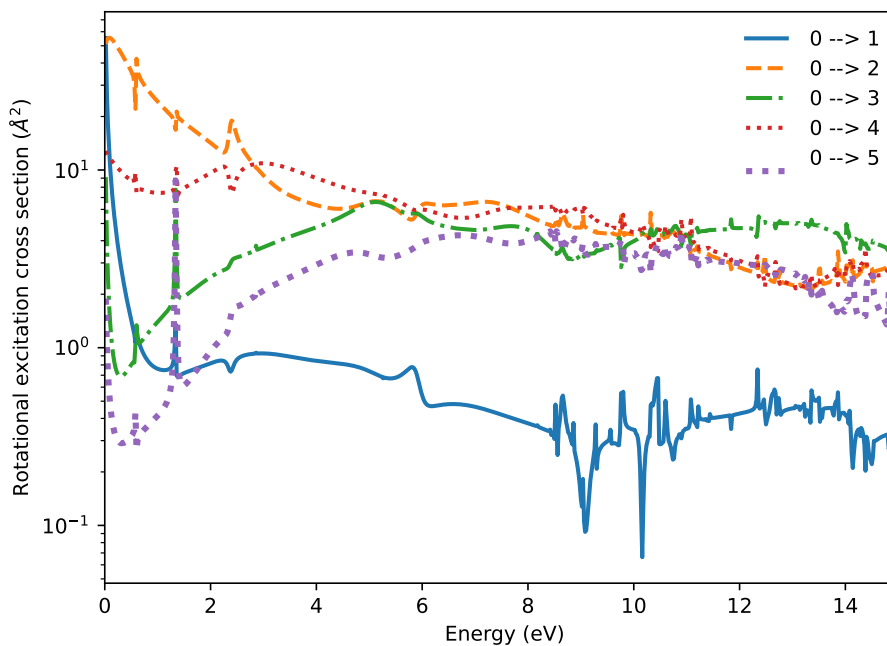


FIG. 6: Electron-impact rotational excitation cross sections for TiCl<sub>3</sub>.

## Electron-impact ionization

The total electron-impact ionization cross section for  $\text{TiCl}_3$ , calculated using the Binary Encounter Bethe method, is shown in Fig.7. Partial ionization cross sections could not be calculated for  $\text{TiCl}_3$  since no appearance thresholds or mass spectrum data are available in the literature.

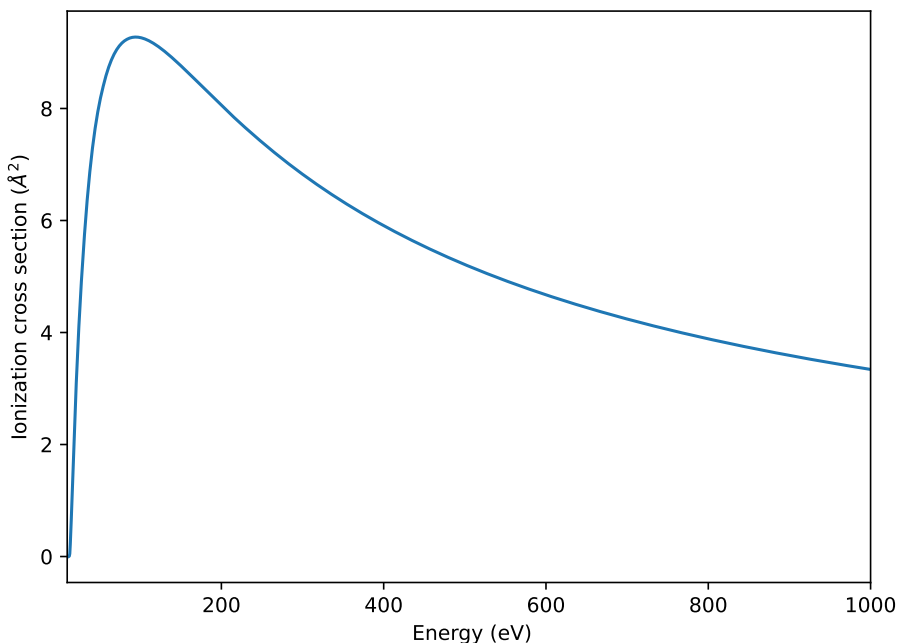
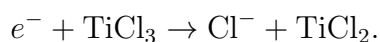


FIG. 7: Total ionization cross section for  $\text{TiCl}_3$ .

## Dissociative electron attachment

The electron-impact dissociative electron attachment cross section for  $\text{TiCl}_3$  is shown in Fig.8. The main electron attachment process is



## Calculation Details

Quantemol Electron Collisions (QEC *version* 1.4) is a user-friendly software package designed for *ab initio* electron-molecule scattering calculations [2]. It is based on the UKRmol and UKRmol+ molecular *R*-matrix suite of codes [3–5] that have been optimised

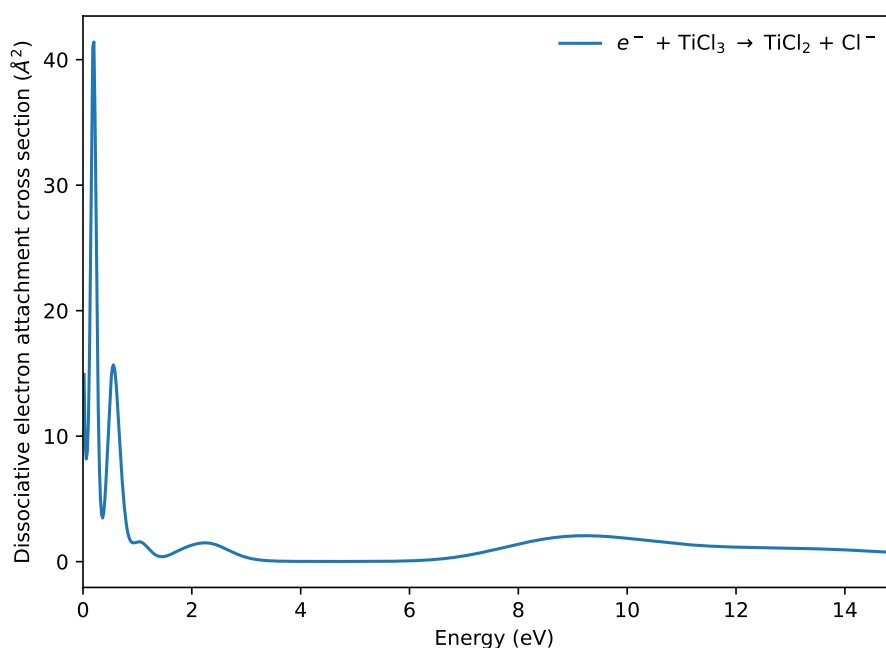


FIG. 8: Dissociative electron attachment cross section for  $\text{TiCl}_3$ .

over many years for the efficient provision of accurate cross section data. The structure of the target molecule is calculated using the Molpro quantum chemistry package [6], whose output is then used by QEC in the subsequent cross section calculation.

QEC calculations are carried out using a convenient Graphical User Interface (GUI). The first stage of the calculation involves the molecular geometry description. To do this, the user can select from a variety of basis sets in which to expand the wavefunctions, and can also choose target orbitals at both the Hartree-Fock Self-Consistent Field (HF) and Multi-Configurational Self-Consistent Field (MCSCF) levels of detail. Subsequently, the user can carry out scattering calculations using Static Exchange (SE), Static Exchange with Polarization (SEP), or close-coupling (CC) methods. Hartree-Fock orbitals are used for scattering calculations with SE and SEP, while MCSCF orbitals are necessary for calculations using close coupling.

The  $\text{TiCl}_3$  molecule contains 73 electrons, belongs to the  $C_{2v}$  point group in its equilibrium geometry, and the ground state is a  $^2A_1$  state. The calculations performed in this work used the def2-SVP basis set. All cross sections were calculated using the close-coupling method, and MCSCF orbitals. These calculations used an active space comprised of 9 active electrons in 8 active orbitals, as described in Table III. An  $R$ -matrix sphere radius of 12 Bohr was used to confine the  $\text{TiCl}_3$  molecule in all calculations.

In QEC, electron-impact ionization cross sections are calculated using the Binary-



Ground state	$(1 - 18a_1, 1 - 6b_1, 1 - 11b_2, 1 - 2a_2)^{73}$
Closed orbitals	$(1 - 16a_1, 1 - 5b_1, 1 - 10b_2, 1a_2)^{64}$
Open orbitals	$(17 - 18a_1, 6 - 7b_1, 11 - 12b_2, 2 - 3a_2)^9$

TABLE III: Active space used for  $\text{TiCl}_3$ .

Encounter-Bethe method [7], in which the cross section,  $\sigma_{BEB}$ , is given by

$$\sigma_{BEB} = \frac{S}{t + u + 1} \left[ \frac{1}{2} \left( 1 - \frac{1}{t^2} \right) \ln t + 1 - \frac{1}{t} - \frac{\ln t}{1 + t} \right], \quad (1)$$

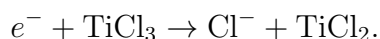
where  $t$ ,  $u$ , and  $S$  depend on the binding energy  $B$ , the kinetic energy  $T$ , the potential energy  $U$ , and the occupation number  $N$  as:  $t = T/B$ ,  $u = U/B$ , and  $S = 4\pi a_0^2 N R^2 / B^2$  ( $a_0$  is the Bohr radius and  $R$  is the Rydberg constant). If  $t < 1$ , then  $\sigma_{BEB} = 0$ .

The dissociative electron attachment (DEA) cross sections were calculated using the DEA estimation method described in Ref. [8]. A vibrational frequency of  $1000 \text{ cm}^{-1}$  and an electron affinity of 3.61 eV was used for Cl.

The neutral dissociation cross sections are computed by summing the excitation cross sections, since the potential energy curves demonstrate that all excited states contribute to dissociation.

## Conclusions

In the present work, we calculated *ab initio* cross sections for the electron-scattering processes of  $\text{TiCl}_3$ . The neutral dissociation cross sections were computed by summing the excitation cross sections. For plasma simulation purposes, it is advised that one should use either the distinct excitation cross section provided or the total dissociation cross section. The dissociative electron attachment cross sections were computed for the following electron attachment processes in  $\text{TiCl}_3$ , yielding the dominant anion species  $\text{Cl}^-$  through the reaction:



## How to cite this work

Please use the following reference to cite the data produced in this report:

- G. Armstrong, *private communication* (2024).

The following references should be used for QEC:

- B. Cooper, M. Tudorovskaya, S. Mohr, A. O'Hare, M. Hanicinec, A. Dzarasova, J. D. Gorfinkiel, J. Benda, Z. Mašín, A. F. Al-Refaie, P. J. Knowles, J. Tennyson, *Atoms*, **7** 97 (2019).

The following references should be used for UKRmol+:

- Z. Mašín, J. Benda, J. D. Gorfinkiel, and A. G. Harvey, *Comput. Phys. Comm.* **249** 107092 (2020).
- J. Tennyson, *Phys. Rep.* **491** 29 (2010).

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- [1] Pubchem identifier:CID 62646, <https://pubchem.ncbi.nlm.nih.gov/compound/62646> (2024).
- [2] B. Cooper, M. Tudorovskaya, S. Mohr, A. O'Hare, M. Hanicinec, A. Dzarasova, J. D. Gorfinkiel, J. Benda, Z. Mašín, A. F. Al-Refaie, P. J. Knowles, and J. Tennyson, Quantemol Electron Collisions (QEC): An enhanced expert system for performing electron molecule collision calculations using the R-matrix method, *Atoms* **7**, 97 (2019).
- [3] J. Tennyson, Electron–molecule collision calculations using the R-matrix method, *Physics Reports* **491**, 29 (2010).
- [4] J. M. Carr, P. G. Galiatsatos, J. D. Gorfinkiel, A. G. Harvey, M. A. Lysaght, D. Madden, Z. Mašín, M. Plummer, J. Tennyson, and H. N. Varambhia, UKRmol: a low-energy electron- and positron-molecule scattering suite, *Eur. Phys. J. D* **66**, 58 (2012).
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- [6] H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, and M. Schütz, Molpro: a general-purpose quantum chemistry program package, *WIREs Computational Molecular Science* **2**, 242 (2012).
- [7] Y.-K. Kim and M. E. Rudd, Binary-encounter-dipole model for electron-impact ionization, *Phys. Rev. A* **50**, 3954 (1994).
- [8] J. J. Munro, S. Harrison, M. M. Fujimoto, and J. Tennyson, A dissociative electron attachment cross-section estimator, *Journal of Physics: Conference Series* **388**, 012013 (2012).