

“Recommended” cross sections for electron collisions with molecules[★]

Mi-Young Song¹, Jung-Sik Yoon¹, Hyuck Cho², Grzegorz P. Karwasz^{3,a}, Viatcheslav Kokoouline⁴, Yoshiharu Nakamura⁵, and Jonathan Tennyson⁶

¹ Plasma Technology Research Center, National Fusion Research Institute, 814-2, Osikdo-dong, Gunsan Jeollabuk-do 573-540, South Korea

² Department of Physics, Chungnam National University, Daejeon 305-764, South Korea

³ Faculty of Physics, Astronomy and Applied Informatics, University Nicolaus Copernicus, 87-100 Toruń, Poland

⁴ Department of Physics, University of Central Florida, Orlando, FL 32816, USA

⁵ 6-1-5-201 Miyazaki, Miyamae, Kawasaki 216-0033, Japan

⁶ Department of Physics and Astronomy, University College London, London WC1E 6BT, UK

Received 29 October 2019 / Received in final form 4 February 2020

Published online 24 March 2020

© The Author(s) 2020. This article is published with open access at [Springerlink.com](https://www.springerlink.com)

Abstract. The procedures for constructing recommended sets of cross sections for electron scattering on molecules are described. Possible sources of errors in total and partial cross section measurements are discussed. Examples when the theory successfully supports and/or substitutes measurements are given. The target molecules discussed comprise CH₄, C₂H₂, NF₃, N₂O, NO₂ and H₂O.

1 Databases

Closer and closer deadlines for the peaceful use of thermonuclear energy [1], recent discoveries in astrochemistry [2] and the demands of studies using technological plasmas [3] have combined to trigger renewed interest in electron-molecule scattering.

Numerous recommended sets of cross sections for electron scattering on atoms and molecules are available in the literature and on the internet. These cross section sets usually evolved from national centers of research. One of first comprehensive internet collections of electron-scattering cross sections was that that settled by Art Phelps, hosted for some time at Oak Ridge and NIST [4,5], and now transferred to the France-based LXCat project [6]. National databases comprise the early French Gaphyor system [7], now not active, Belgrade BEAMDB [8] and several fusion-related projects: ADAS (University of Strathclyde, UK) [9], the recently re-formatted Japanese NIFS database [10], Korean NFRI [11], Chinese CAMDB [12], and the IAEA-based AMDIS [13]. This growing amount of data-collecting centers make emerge meta-centers, that collect links to specific databases; we mention Weizmann

center [14], the EU-funded virtual atomic and molecular data centre [15], the already mentioned France-based but with a wide international collaboration LXCat [6] and the Quantemol Database (QDB) aimed at chemistries for technological plasmas [16].

The first experiments on electron scattering in gases were performed (by Lenard [17]) even before the official discovery of electron by Thomson in 1897, so the history of printed reviews of data is also long. Major milestones were summarized by Ramsauer and Kollath [18], Brode [19], Bederson and Kieffer [20], Trajmar et al. [21] and Karwasz et al. [22]. Encyclopedic issues were published, among others, by Landolt-Börnstein [23]. Numerous research reports have also been published by the data centers listed above.

Significant papers can be divided into two groups: discussing several processes for a given gas or dealing with a single process (like the ionization [24]) in different species. For the latter we mention the binary-encounter Born-Bethe model for the total ionization cross sections by Kim and Rudd [25,26], which is available on-line from NIST database [27].

An extensive series of papers on cross sections on molecules of atmospheric interest was published by Itikawa and co-workers (e.g. [28]), and on molecules of plasma and semiconductor processing by Christophorou and Olthoff (e.g. [29]). The methodology of these papers [30] is based essentially on a critical comparison of existing experiments, that used predominantly beam techniques.

A different approach is adopted in studies based on measurements of transport coefficients in electron swarms; this method originated with Townsend and was developed

[★] Contribution to the Topical Issue “Low-Energy Positron and Positronium Physics and Electron-Molecule Collisions and Swarms (POSMOL 2019)”, edited by Michael Brunger, David Cassidy, Saša Dujko, Dragana Marić, Joan Marler, James Sullivan and Juraj Fedor.

^a e-mail: karwasz@fizyka.umk.pl

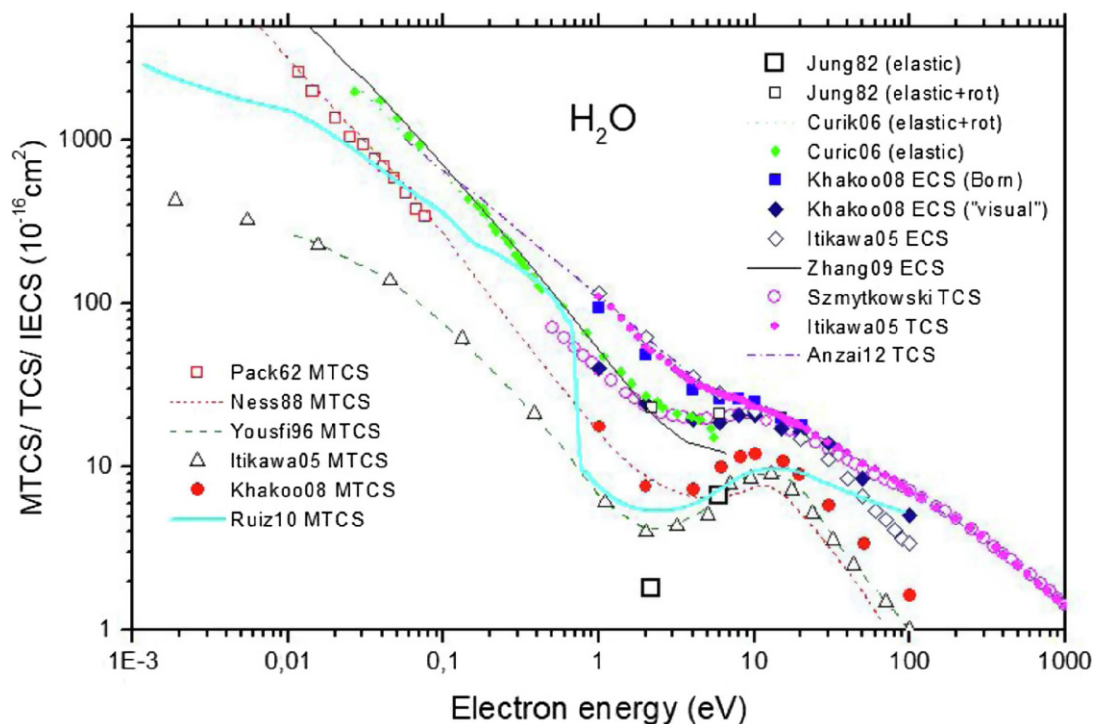


Fig. 1. Example of difficulties in interpreting cross sections definitions: MTCS of Pack et al. [44] and Ness and Robson [45] include the rotational excitation, while that of Ruiz-Vargas et al. [47] no. Theoretical cross sections (*R*-matrix calculations) [54] make distinction between IECS and MTCS without and with the rotational cross section. Experimental TCS [49] that do not resolve the rotational excitation is clearly underestimated.

in particular by Huxley and Crompton [31] (see reviews by Dutton [32] and Gallagher et al. [33]). The swarm-based analysis usually presents self-consistent sets of cross sections for several processes (momentum transfer, rotational, vibrational and electronic excitation, etc.). These cross section sets are used as input to Boltzmann (or Monte Carlo) models that calculate transport coefficients to be compared with the experiments [34–36]. The weak point of some of those sets is that, in the case of a limited base of experimental transport coefficients (only the pure target molecule, a narrow energy range, only some of possible coefficients analysed) the derived sets of cross sections can be non-unique. Additionally, the interpretation of the derived cross sections can vary from author to author. This is the case, for example, of total, momentum transfer and elastic cross sections in H_2O , shown in Figure 1, which we discuss below.

The present group, defined by the authors of this paper, was born out of the data needs of models of fusion edge plasmas for the ITER experiment, so our first papers were dedicated to hydrocarbons [37,38]. However our more recent compilations include atmospheric species [39,40] and gases with potential industrial applications, like NF_3 [41]. The expertise in the group is deliberately mixed consisting of theory, beam and swarm experiments and plasma applications. As a result our analysis is not limited to existing experiments but builds on it, when needed, using theory; beam and swarm results are also tensioned against each other. Consistency of the derived cross-section sets is further checked by Boltzmann analysis (and com-

pared to transport coefficients, if available). Anyhow, we are far from calling the data presented as recommended cross sections.

In this work we discuss issues that have emerged during our analysis of experimental (and theoretical) cross section to derive recommended data sets. Some questions are related to specific targets, like the difficulties in measurements (and calculations) of cross sections in polar molecules, some are related to the drawbacks of given experimental techniques in general.

2 Definitions

By the gross total cross section (TCS) we intend the overall probability of an electron to be scattered, via any channel – elastic or inelastic. TCS includes all scattering processes so it constitutes an upper limit for the sum of all partial cross sections and if correctly used (and measured) may serve as a normalization procedure for partial processes.

From its definition the elastic cross section should not include any inelastic process. However, in measurements of elastic cross sections using beams it is difficult to discern electrons scattered with a small change in energy, which means for the majority of molecules any rotational excitation (or rotational de-excitation). Therefore, in beam experiments the measured cross sections are called vibrationally elastic (or elastic + rotational). These general definitions are valid for all targets.

Only in few experiments (H_2O , CH_4) performed with particularly good energy resolution (some as low as 10 meV) the rotational-excitation cross sections have been separated from elastic ones [42]. Such a result for H_2O is shown in Figure 1. The integral elastic cross section, IECS (open squares in Fig. 1) appears to exhibit a Ramsauer-Townsend minimum, like that in CH_4 [43], in spite of the fact that water is a polar molecule.

Unfortunately, measurements of transport coefficients are also not sensitive enough to discern the rotational excitation: electrons in a swarm continuously induce the rotational excitations and de-excitations of molecules, so the net energy loss is essentially zero. Depending on the choice of rotational excitations, the derived MTCSS [44–47] may differ significantly (see Fig. 1). In practical terms it is relatively straightforward to use theory to generate rotational excitation cross sections (e.g. [48]).

On the other hand, the experimental TCS [49] which should be the upper limit for all cross sections in Figure 1 is lower than the integral elastic cross section (IECS) from the recent beam experiment [50]. As some authors [49] repeated their measurements in two different experimental configurations, the discrepancies must result from some systematic errors.

3 Total cross-sections

Experiments with electron beams are, potentially, the most precise as it is possible to measure separately total, integral elastic, integral vibrational, electronic-excitation and ionization cross sections just by changing the energy resolution of the post-collision energy analyzer. However, as these cross sections should be obtained by integrating differential cross sections, DCS, numerous experimental problems arise, the normalization procedures being the most complex. In practice, only TCS can be measured in an absolute manner in beam-attenuation experiments. Measurements by the attenuation method are conceptually very simple, requiring only the knowledge of the pressure (and temperature) in the scattering chamber. Therefore, for many targets, like CH_4 [37] the agreement between different laboratories is excellent (within 5%). However, in some cases total cross sections can suffer from systematic, difficult to avoid errors. One of these errors is the angular resolution: the entrance and exit orifices in the scattering cell can not be too small, so a fraction of electrons (those scattered under small angles) will be counted as non-scattered, lowering the measured cross section.

This error is particularly acute in polar molecules at low energies, where the direct (i.e. non-resonant) rotational excitation is big and at high energies, where several inelastic channels (ionization, electronic excitation) are open. DCSs for these processes (and especially for the electronic excitation into the dipole-allowed transitions) are forward-centered. In Figure 2 we show the discrepancy between the experimental total cross sections [51] and theories [52]. Theories (and semi-classical estimations) predict a $1/E$ slope of the total cross section in the very low-energy range while the experiments differ from this dependence.

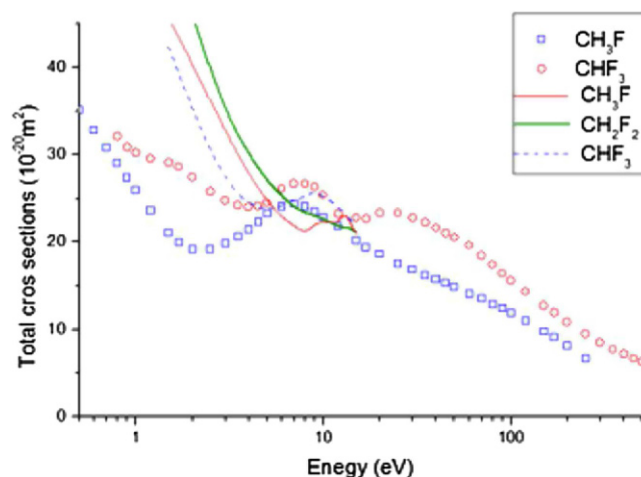


Fig. 2. Comparison of experimental [51] and theoretical [52] TCS. For all three polar targets (dipole moment 1.65 D, 1.85 D and 1.97 D, for CHF_3 , CH_3F and CH_2F_2 , respectively) the experiment is lower than the theory. The discrepancy could result from a limited (1 msr) angular resolution of the experiment.

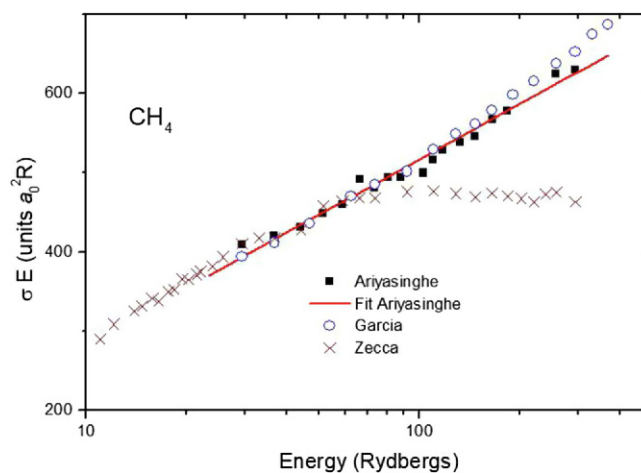


Fig. 3. The so-called Born-Bethe plot of total cross-section (semi-log dependence of TCS on energy) shows clearly that measurements without retarding field analyser [56] underestimate the TCS [57,98].

As shown recently for water by Kadokura et al. [53], experiments with well defined, high angular resolution can discern even the electrons rotationally scattered into small angles. In the case of H_2O , this rises the experimental TCS significantly, towards the theoretical values (see Ref. [54]).

The upper-energy limit of the beam-derived TCS is also subject to underestimation. The Trento TCS apparatus, with which numerous electron (and positron) molecule cross sections have been measured up to collision energies of 4 keV [55], was not equipped with the energy analyzer at the exit of the scattering cell. As discussed previously [56], the expected error in the elastic channel was of few per cent, while in the inelastic channel it is much higher. Thanks to a more recent experiment [57] we can evaluate

the underestimation of TCS in Trento measurements as some 30% at the high-energy (3 keV) limit (see Fig. 3). On that plot we present, apart from experimental data, the so-called Born-Bethe dependence, according to which the TCS can be at high energies approximated by the formula

$$\text{TCS} = A \log \left(\frac{E}{R} \right) + \frac{B}{E},$$

where R is the Rydberg constant.

We see clearly that measurements without retarding-field analyzer at the exit of the scattering cell depart from the predicted energy dependence above some 1 keV. On the other hand, this method could be used to roughly estimate of the total inelastic cross section at high energies.

3.1 Elastic cross-sections

Integral elastic cross sections (IECS) need differential cross sections as the input data and, then, some extrapolation of DCS towards angles inaccessible in direct measurements. This extrapolation, together with normalization procedures for the estimation of the target gas density, is the main source of errors in IECS. The uncertainties usually declared in IECS measurements are 20–30%. However, for some molecular targets like H_2O clearly bigger discrepancies exist between different experimental sets.

The differences that arise from extrapolation procedures in the same experiment are shown in Figure 1. The IECS labelled as Khakoo visual [50] uses a simple polynomial to extrapolate DCS down to zero scattering-angle. The IECS Khakoo Born uses the Born extrapolation: the difference at 1 eV between the two sets is a factor of three. The reason is that it is not possible to separate out the rotational excitation, which is strongly forward peaked.

In case of such big discrepancies theory must be used. Zhang et al. [54] derived, after an extensive discussion of possible methods, an analytical formula for low-angle corrections of elastic and rotationally inelastic DCS (both for positrons and electrons). This triggered further experimental work [53], including detailed studies of the angular resolution effect in TCS, what also allows one to evaluate, a-posteriori, other experimental results [58].

3.2 Vibrational cross-sections

Vibrational excitation (VE) is usually measured by beam techniques along with the elastic scattering and, for this reason is subject to similar possible systematic errors. Further, the near-to-threshold region is rarely accessible to direct measurements unless special precautions are taken [59]. Nevertheless, as seen in the case of CH_4 the agreement between different experiments [59–62] is fairly good.

This case is not typical as agreement between theory and experiment for polyatomic molecules is generally poor (see Fig. 4). The Born approximation gives pretty good results for infrared active modes near threshold (even for positrons [63]), but different theories diverge in predicting

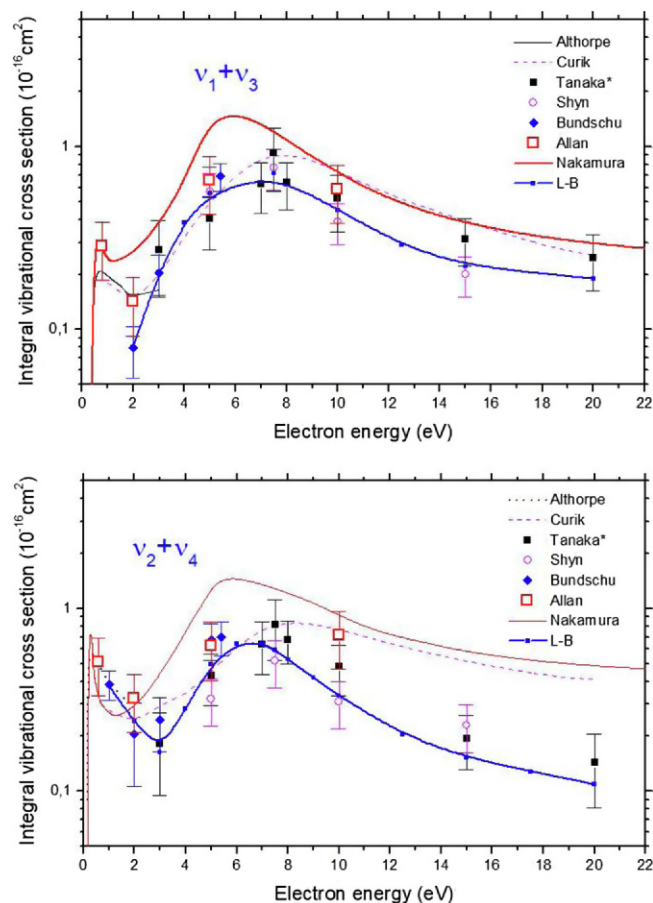


Fig. 4. Comparison between theory [99,100], beam experiments [59–62] and swarm-derived [37] vibrational excitation cross section for methane. Swarm-derived values are a factor of two to three higher than beam measurements: this reflects the role of vibrational overtones in the energy balance of swarms. L–B stands for preferred values by Brunger, Buckman and Elford from the Landolt–Börnstein review [101].

VE at resonances. Resonance enhanced VE cross sections are often much larger and special theoretical procedures are required to compute them (e.g. [64]).

Furthermore, it is not easy to cross-check the VE cross sections from beam and swarm experiments; generally the latter give higher values for the cross sections (see Fig. 4). This is because in the swarm analysis the total energy-loss (including overtones) is significant, while the data shown in Figure 4 (for example) are the fundamental modes only, without overtones. The excitation to the overtones, even if much weaker, results in higher energy loss. So, as an operative recipe, for the sake of comparison with theories, the beam experiments are significant, while for plasma modeling the swarm-derived cross sections are more appropriate: users of data must be aware of this non-uniqueness.

3.3 Resonances

Semi-empirical comparisons of shape resonances in molecules show that the VE may bring a high contribution

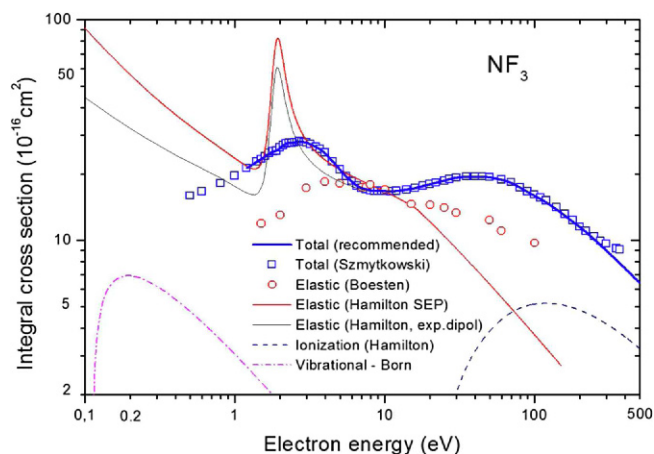


Fig. 5. Total, integral elastic, counting ionization and vibrational excitation (Born approximation, using the dipole moments from [102]) for NF_3 . The maxima in TCS and IECS are significantly shifted: new theoretical approaches that include the VE in the resonance would be needed.

to the TCS. In iso-electronic molecules N_2 [65] and CO [64] at about 2 eV ($^2\Pi$ shape resonance) the VE amounts to 1/6 of TCS, while at similar resonances in N_2O , CO_2 and OCS to as much as 1/3 of TCS [66]. Clearly, theories must go beyond the fixed-nuclei approximations to estimate correctly the amplitude (and the position) of shape resonances. This is particularly important for molecules in which the VE transition dipole moments are high, like CF_4 or NF_3 (see Figs. 5 and 6).

In Figure 5 we compare the theoretical (R -matrix) [67] and experimental TCS and IECS for NF_3 . The theory correctly predicts the position of the resonance as seen in TCS, but overestimates its magnitude (due to the fixed-nuclei approach). However, the maximum in IECS is shifted towards a higher energy, while at the position of the resonance a maximum of VE was measured [68] (see Fig. 6).

Figure 5 shows also that a serious discrepancy exists between the experimental TCS and theoretical IECS in the very low energy range. A part of this difference can be ascribed to the angular resolution but the theory is also quite sensitive to the choice of the dipole moment used. And at energies of tenths of eV an enhancement of VE for infrared active modes is predicted by the Born approximation but it was not seen in the experiment [69].

A similar shift between maxima in TCS and IECS is seen in another fluorine-containing small molecule, CF_4 (see Fig. 6). The maximum of TCS appears at about 9 eV while two weak maxima are present in IECS at 4 eV and 12 eV.

3.4 Electronic excitations

The measurements of electronic excitation cross sections are subject to the same uncertainties as the elastic ones. Additionally, for targets with overlapping vibronic bands, difficulties arise in deconvolution of the spectra, so errors can rise in assigning the states to a given loss channel.

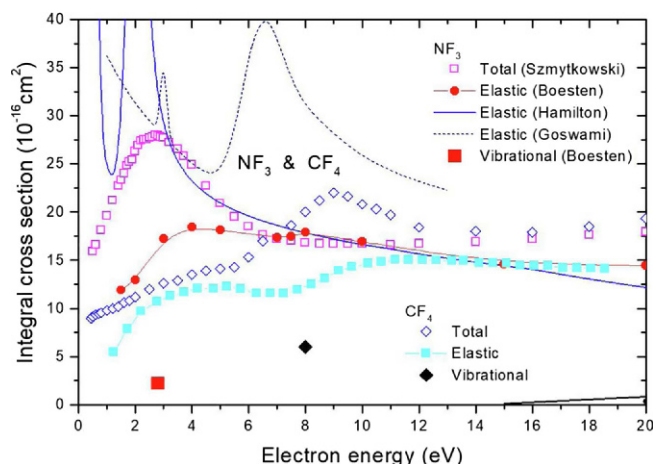


Fig. 6. Comparison of total and integral elastic cross sections in NF_3 and CF_4 . Surprisingly, two maxima in IECS are predicted by Goswami et al. [103] in NF_3 , even if much sharper than the experimental TCS (see Fig. 5). Like in NF_3 , the maximum of TCS in CF_4 corresponds to the maximum in the VE cross sections (which amounts to some 25% there). More experimental and theoretical studies are needed for fluorine-containing molecules, also because of their importance in etching processes in semiconductor industries.

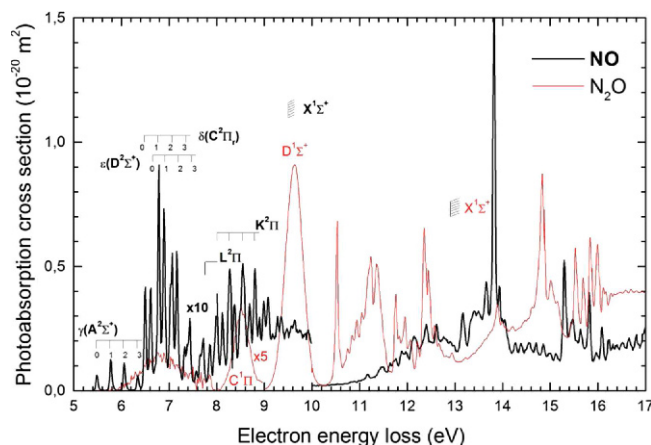


Fig. 7. Differential cross section for scattering into zero-angle vs. the energy loss [70,104]. Such spectra correspond to photoabsorption cross sections (see [70]).

In Figure 7 we show the DCS for electron scattering at zero angle against energy loss. Such spectra, with the zero momentum transferred to the target can be directly compared with photoabsorption cross sections (see [70] for details). As seen from that figure, the energy-loss pattern is particularly dense in NO , so, for example, the L state is difficult to separated from the K state.

Another way to distinguish specific states is to follow the integral electronic-excitation cross section (IEECS) vs the collision energy: dipole-allowed IEECS fall slowly with the energy, at high energies like $1/E$ while the forbidden states this dependence is much steeper.

Recently an additional hint on how to get the correct normalization of IEECS came from the scaled Born-Bethe

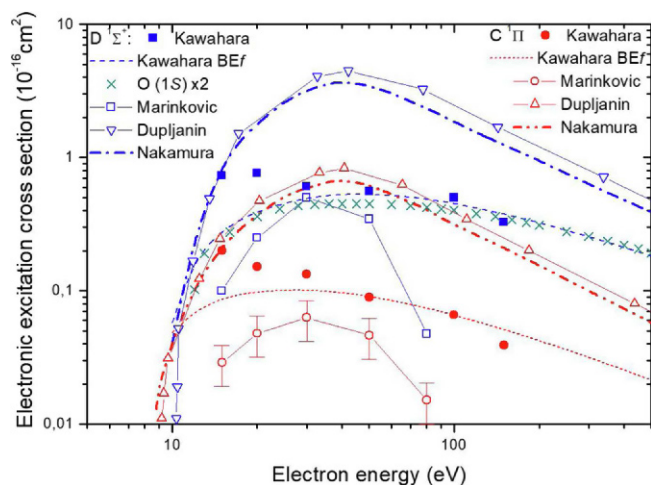


Fig. 8. Integral cross sections for electronic excitation into the dipole-allowed C and D states in N_2O (broad peaks in the energy-loss spectra in Fig. 7). The beam experiments, in fair mutual agreement (Kawahara et al. [72] and Marinković et al. [105]) give lower cross sections than swarm evaluations. This is, similar to the case of the vibrational excitation and is due to the higher energy loss that overtones (i.e. higher vibronic states) brings to the swarm energy balance.

(BEf) model [25], which was originally developed for the electron-impact ionization, see below. The BEf method gives an analytical formula for optically allowed IEECS but requires the optical-oscillator strength. These, in turn, can be obtained both by optical and theoretical methods (a comprehensive discussion for the C and D states in N_2O was given by Xu et al. [71]). For N_2O this considerations induced us to recommend the f -BEB cross sections [72].

The IEECS derived from measurements of transport coefficients [39,73] show identical energy dependence (see Fig. 8), but are a few times higher. The cause is the same as for VE: the energy balance of swarms requires the inclusion of higher vibronic states, with the energy-loss higher than the mere threshold for the excitation. To perform a full analysis one should use cross sections for optical excitation to all the vibronic states; these data are usually not available (see for example [74]).

In summary, different cross checks allow one to get reliable IEECS, but still only for a few molecules. Otherwise, theory has to be used. However, comparisons for different targets indicate that the electronic excitation constitutes not more than a few (5%) of the TCS. At high energies it is the ionization cross sections which dominate, together with the elastic scattering.

3.5 Ionization cross-sections

Ionization cross sections, like TCSs, can be measured using relatively simple methods, giving therefore in some cases recommended cross sections with an uncertainty below 10%.

However, when comparing data one should distinguish between “gross total” and “counting total” cross section.

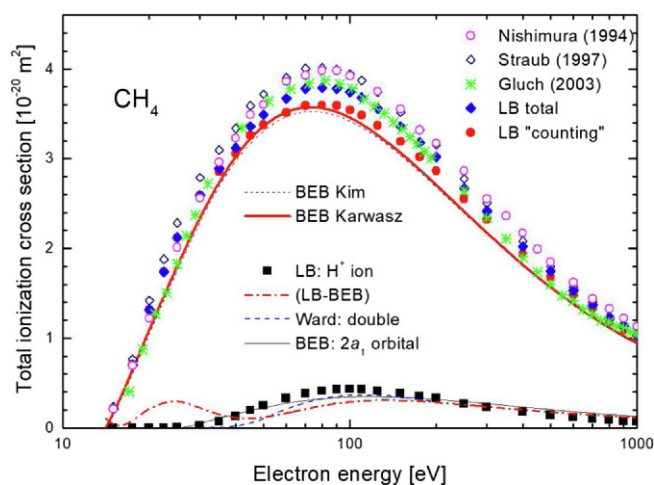


Fig. 9. Gross total and counting total ionization in CH_4 : the difference lies in the double counting of signals from events in which a pair of ions are formed. H^+ is the good example: as shown by Ward et al. [77], at 200 eV half of the H^+ ions arise from double ionization. Two BEB model calculations are given [67,106]; for the latter we give also the contribution from the $2a_1$ molecular orbital.

The gross total cross section is measured as the total current of ions created in the collision. As some ions can be formed with a double charge (if the atom loses two electrons), the total current of ions overestimates the number of ionization events which are measured by the total counting cross section. This difference is visible, for example, for noble gases: in Ar at 200 eV the double ionization amounts to 6% of the total counting ionization cross section [75].

In the case of molecules, the double ionization is much smaller, in N_2 at 200 eV is only 1% of total counting [76] and no doubly-charged ions are reported for CH_4 . Instead of doubly charged ions, a single ionization event can lead to formation of a pair of ions which, if collected as a total ion charge, overestimates the counting ionization cross section. This is more difficult to distinguish, even in experiments with mass spectrometers. Only recently have coincidence measurements [77] allowed one to distinguish between single and double ionization events: in CH_4 the yield of H^+ ions in double ionization collisions at 200 eV equals that from the single ionization. Therefore, half of the H^+ signal has to be subtracted from the experimental gross total ionization cross section to yield the counting ionization (see Fig. 9).

Additionally, a useful indication in choosing recommended ionization data is the binary-encounter Bethe-Born (BEB) model [26] as for most molecules it gives a good approximation to the total counting ionization cross section. In some case this can be better than the previously recommended experimental data (see Fig. 9). However, even if the BEB model gives reliable total ionization cross sections, it has not yet been applied to partial cross sections, even though the BEB total ionization cross section is obtained as the sum of the contributions of electrons kicked-out from single orbitals. A trial [67] performed for NH_3 partial ionization, using the NIST experimental mass spectrometry data to get partitioning is quite

promising. An ambitious goal would be to derive directly partial ionization cross sections for single orbitals, but the BEB model does not include any possible post-collisional interactions.

3.6 Other processes

A complete set of cross sections must also include other processes. The experimental evaluations of the rotational excitation are scarce, so the theory is needed. For C_2H_2 we presented [38] a set of differential cross sections for $j = 0 \rightarrow j' = 0, 2, 4$ at collision energies 0.1–10 eV, obtained using the Quantemol-N [78] implementation of the UK molecular R -matrix suite of programmes [79]; hardly any theory [80] or experiment exists to compare against. Similar calculations for NF_3 (for five rotational transitions) (see [41]), showed clearly the resonant state at about 2 eV. This is also the case of the shape resonance in N_2O , well pronounced in the rotation-elastic channel, for all $j = 1 \rightarrow j' = 1 - 5$ transitions (see [39]). In contrast, no resonance appears in the same channels in NO_2 between 0.2 and 3 eV, even though an alternative calculation [81] claimed two sharp resonances in the elastic cross section.

The same set of programmes, based on the UK R -matrix code have been used to obtain IEESC for targets in which no experiments are available, like NF_3 [41] and NO_2 [39].

Experimental data for the dissociation into neutrals are also relatively scarce. Direct measurements were performed only in few cases like for fluoromethanes [82], where fluorine radicals were captured in the getter of the vacuum pump, or for oxygen containing molecules, N_2O [83] and H_2O [84], via detection of metastable 1S atomic oxygen. In N_2O the experiment of LeClair and McConkey [83] gave the cross section for the dissociation into $O(^1S)$ which amounts exactly to half of the IEESCS to the D state, Figure 8.

Indirect experimental methods to evaluate dissociation into neutrals are based on measurements of optical emission from molecular fragments. Both swarm [85] and beam techniques [86] have been used. However, these methods bring several difficulties including the need for normalization for the gas density and for the optical signal collection, the need to sum over all vibronic states and the possibility of cascading from higher excited states. Therefore, in some cases high “normalization” factors must be used, see the discussion for N_2O in our recent paper [39].

Theoretical cross sections for dissociation into eight neutral channels in NF_3 have been obtained by R -matrix method by Hamilton et al. [67] and see also [41], but we are not aware of any experiment to compare with.

Electron attachment cross sections are measured with a great success by swarm techniques that are sensitive to negative ions. However, to distinguish the ions formed, mass spectrometers must be used. Similarly as in the ionization, problems with the collections of ions and with their distinction in the case of close masses (like O^- and OH^- from H_2O [87]) can alter the spectra. Therefore, in order to give recommended values, a careful analysis of experimental conditions must be done: it can happen that early data [88] are more reliable than recent experiments.

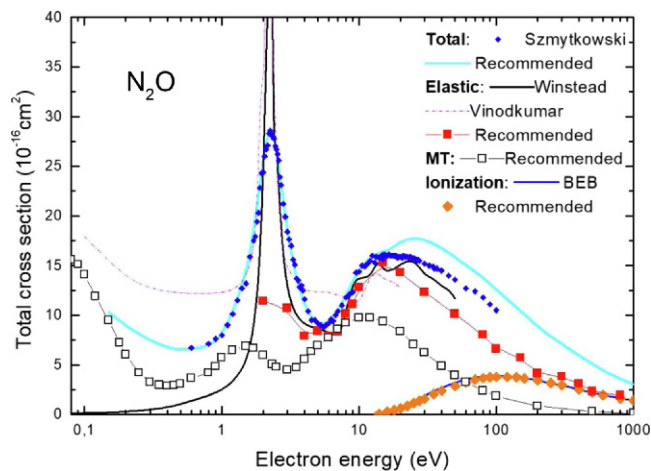


Fig. 10. Comparison between selected experiments, theories and recommended [39] cross sections for N_2O . Total experimental [94]; elastic: Schwinger multichannel [90], Q-mol without Born correction [89]; ionization: BEB method [26].

4 Conclusions

The search for recommended cross sections should, if possible, use many different experiments performed with complementary method (as is often the case for electron impact ionization). However, even the use of data from different laboratories does not protect from systematic errors. Theoretical methods, in spite of their limitations, are increasing in importance for recommending cross sections.

In Figure 10 we present comparison between some theoretical methods and the recommended cross sections [39] in N_2O : BEB approximation for ionization [26], Quantemol-N package [89] and Schwinger variational method [90] for the elastic cross section. The BEB model approximates the total ionization cross section within 5%; the job is much tedious with the elastic cross section. Calculations (see also [91–93]), using the fixed-nuclei approach generally overshoot the low-energy resonant maximum of the TCS (and of the elastic cross section). Outside the resonance the Schwinger multichannel method [90,92] agrees better with our [39] recommended cross sections than the Quantemol calculation of Vinodkumar and Barot [89]. In turn, the Quantemol calculations correctly predict the low-energy rise of the total and momentum transfer cross section. Clearly, both refinements of experiments, such as better angular resolution as the beam measurements [94] fall below the theory, and the extension of calculations towards lower energies (to get matching with swarm-derived momentum transfer cross sections) are needed.

A series of review papers is under publication by our group, starting from CH_4 [37], C_2H_4 [38], NF_3 [41] to nitrogen oxides (NO , N_2O , NO_2) [39] and most recently water vapour [40]. The main novelty of our approach is the extensive referring to the theory. The UK R -matrix code (and the Quantemol package) proved to be the most versatile tool to calculate elastic cross sections both in molecules dominated at low energies by resonances

like NF_3 [67] and in polar targets like H_2O [54]. The R -matrix codes allowed also to evaluate electronic excitation in nitrogen oxides (work in progress). For validation of total ionization cross sections we use with success the Born-Bethe binary encounter model [26]; however, application of this model to partial ionization cross sections [67] still requires some experimental input. We note that both the UK molecular R -matrix codes [79,95] and the associated Quantemol front end [96] have undergone extensive upgrades which should further extend their utility.

Further consistency of the proposed sets is obtained by comparison of cross sections from beam techniques with data derived from swarm experiments, both for pure and (what is even more stringent) mixed gases [37]. A rigorous check would be an output from plasma-modelling projects (and plasma experiments), conforming or not the recommended cross sections.

Returning to the title of the paper: at present, for quite few targets (such as noble gases) really unique and self-consistent cross section sets can be given. Reciprocal criticism between different theoretical and experimental approaches stimulates the extension this work yielding complementary cross sections which, importantly, include upper limits on systematic errors, to search for analogies [97] – must continue before the recommended goal is achieved.

This work was partially supported by the National Research Council of Science and Technology (NST) grant by the Korean government (MSIP) No. PCS-17-05-NFRI. All authors contributed to the paper in equal parts. These include the literature search, selection of data, evaluation procedures, group discussions, preparing figures and the manuscript.

Author contribution statement

Song leads the data validation project; Karwasz drafted the article; all authors contributed to the data validation process and editing of the article.

Open Access This is an open access article distributed under the terms of the Creative Commons Attribution License (<https://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

References

1. J.S. Yoon, M.Y. Song, J.M. Han, S.H. Hwang, W.S. Chang, B. Lee, *J. Phys. Chem. Ref. Data* **37**, 913 (2008)
2. A. Tsiaras, I.P. Wladmann, G. Tinetti, J. Tennyson, S.N. Yurchenko, *Nat. Astron.* **3**, 1086 (2019)
3. K. Bartschat, M.J. Kushner, *Proc. Natl. Acad. Sci. U.S.A.* **113**, 7026 (2016)
4. A.V. Phelps, Compilation of electron cross-sections. <http://jilawww.colorado.edu/www/research/colldata.html> (Accessed 1999), <https://www.nist.gov/sites/default/files/documents/srd/jpcrd388.pdf>
5. A.V. Phelps, *J. Phys. Chem. Ref. Data* **19**, 653 (1990)
6. L.C. Pitchford, et al., *Plasma Proc. Polym.* **14**, 1600098 (2017)
7. A Database on the Properties of Atoms, Molecules, Gases and Plasmas, including Chemical Reactions, Laboratoire de Physique des Gaz et des Plasmas (Universit Paris-Sud, France), <http://gaphyor.lpgp.u-psud.fr/>
8. B.P. Marinković, V.A. Srećković, V. Vujčić, S. Ivanović, N. Uskoković, M. Nesić, L.M. Ignjatović, D. Jevremović, M.S. Dimitrijević, N.J. Mason, *Atoms* **7**, 11 (2019)
9. H.P. Summers, M.G. O'Mullane, *AIP Conf. Proc.* **1344**, 179 (2011)
10. M. Emoto, I. Murakami, D. Kato, M. Yoshida, M. Kato, S. Imazu, *Atoms* **7**, 91 (2019)
11. Data Center for Plasma Processes (National Fusion Research Institute, Daejeon, Republic of Korea), <https://dcp.nfri.re.kr/search/index.do>
12. Atomic & Molecular Database (Institute of Applied Physics and Computational Mathematics, Beijing, China), <http://www.camdb.ac.cn/e/>
13. Atomic Molecular Data Services (International Atomic Energy Agency, Vienna, Austria), <https://www-amdis.iaea.org/>
14. Databases for Atomic and Plasma Physics (Plasma Laboratory - Weizmann Institute of Science, Rehovot, Israel), <http://plasma-gate.weizmann.ac.il/directories/databases/>
15. M.L. Dubernet, et al., *J. Phys. B: At. Mol. Opt. Phys.* **49**, 074003 (2016)
16. J. Tennyson, et al., *Plasma Sources Sci. Technol.* **26**, 055014 (2017)
17. P. Lenard, *Ann. Phys.* **456**, 1255 (1895)
18. C. Ramsauer, R. Kollath, *Der Wirkungsquerschnitt von Gasmolekülen gegen über langsamen Elektronen und langsamen Ionen*, in *Handbook der Physik* (Springer, Berlin, 1933), 2nd edition, Vol. 22, Part 2
19. R.B. Brode, *Rev. Mod. Phys.* **45**, 1257 (1933)
20. B. Bederson, L.J. Kieffer, *Rev. Mod. Phys.* **443**, 1601 (1971)
21. S. Trajmar, D.F. Register, A. Chutjian, *Phys. Rep.* **497**, 1219 (1983)
22. G.P. Karwasz, A. Zecca, R.S. Brusa, *Riv. Nuovo Cimento* **24**, 1 (2001)
23. G.P. Karwasz, R.S. Brusa, A. Zecca, 6.1 Total scattering cross sections: datasheet from Landolt-Börnstein – Group I elementary particles, nuclei and atoms, in *Volume 17C: Interactions of Photons and Electrons with Molecules*, edited by Y. Itikawa (Springer-Verlag, Berlin, Heidelberg, 2003)
24. T.D. Märk, Ionization of molecules by electron impact, in *Electron-Molecule Interactions and their Applications*, edited by L.G. Christophorou (Academic Press, 1984), Vol. 1, pp. 251–334
25. Y.K. Kim, *Phys. Rev. A: At. Mol. Opt. Phys.* **64**, 032713 (2001)
26. Y.K. Kim, M.E. Rudd, *Phys. Rev. A: At. Mol. Opt. Phys.* **50**, 3945 (1994)
27. Electron-Impact Cross Section for Ionization and Excitation Database (National Institute of Standards and Technology, Gaithersburg, USA), <https://physics.nist.gov/PhysRefData/Ionization>
28. Y. Itikawa, A. Ichimura, K. Onda, K. Sakimoto, K. Takayanagi, M. Hatano, M. Hayashi, H. Nishimura, S. Tsurubuchi, *J. Phys. Chem. Ref. Data* **418**, 123 (1989)

29. L.G. Christophorou, J.K. Olthoff, *J. Phys. Chem. Ref. Data* **28**, 131 (1999)
30. M. Hayashi, Electron collision cross-sections for molecules determined from beam and swarm data, in *Swarm Studies and Inelastic Electron-Molecule Collisions*, edited by L.C. Pitchford, B.V. McKoy, A. Chutjan, S. Trajmar (Springer-Verlag, Berlin, 1987), p. 167–187
31. L.G.H. Huxley, R.W. Crompton, *The Diffusion and Drift of Electrons in Gases* (Wiley, New York, 1974)
32. J. Dutton, *J. Phys. Chem. Ref. Data* **4**, 577 (1975)
33. J.W. Gallagher, E.D. Beaty, J. Dutton, L.C. Pitchford, *J. Phys. Chem. Ref. Data* **21**, 109 (1983)
34. Y. Nakamura, *J. Phys. D: Appl. Phys.* **43**, 365201 (2010)
35. Y. Ohmori, K. Kitamori, M. Shimozuma, H. Tagashira, *J. Phys. D: Appl. Phys.* **19**, 437 (1986)
36. G.N. Haddad, *Aust. J. Phys.* **38**, 677 (1985)
37. M.Y. Song, J.S. Yoon, H. Cho, Y. Itikawa, G.P. Karwasz, V. Kokoouline, Y. Nakamura, J. Tennyson, *J. Phys. Chem. Ref. Data* **44**, 023101 (2015)
38. M.Y. Song, J.S. Yoon, H. Cho, Y. Itikawa, G.P. Karwasz, V. Kokoouline, Y. Nakamura, J. Tennyson, *J. Phys. Chem. Ref. Data* **46**, 013106 (2017)
39. M.Y. Song, J.S. Yoon, H. Cho, G.P. Karwasz, V. Kokoouline, Y. Nakamura, J. Tennyson, *J. Phys. Chem. Ref. Data* **48**, 043104 (2019)
40. M.Y. Song, et al., *J. Phys. Chem. Ref. Data* (to be submitted)
41. M.Y. Song, J.S. Yoon, H. Cho, G.P. Karwasz, V. Kokoouline, Y. Nakamura, J.R. Hamilton, J. Tennyson, *J. Phys. Chem. Ref. Data* **46**, 043104 (2017)
42. R. Muller, K. Jung, K.H. Kochem, W. Sohn, H. Ehrhardt, *J. Phys. B: At., Mol. Opt. Phys.* **18** 3971 (1985)
43. K. Fedus, G.P. Karwasz, *Eur. Phys. J. D* **68**, 93 (2014)
44. J.L. Pack, R.E. Voshall, A.V. Phelps, *Phys. Rev.* **127**, 2084 (1962)
45. K.F. Ness, R.E. Robson, *Phys. Rev. A: At. Mol. Opt. Phys.* **38**, 1446 (1988)
46. M. Yousfi, M.D. Benabdessadok, *J. Appl. Phys.* **80**, 6619 (1996)
47. G. Ruiz-Vargas, M. Yousfi, J. de Urquijo, *J. Phys. D: Appl. Phys.* **43**, 455201 (2010)
48. A. Faure, H.N. Varambhia, T. Stoecklin, J. Tennyson, *Mon. Not. R. Astron. Soc.* **382**, 840 (2007)
49. C. Szmytkowski, *Chem. Phys. Lett.* **136**, 363 (1987)
50. M.A. Khakoo, H. Silva, J. Muse, M.C.A. Lopes, C. Winstead, V. McKoy, *Phys. Rev. A: At. Mol. Opt. Phys.* **78**, 052710 (2008)
51. C. Szmytkowski, A. Krzysztofowicz, *Chem. Phys. Lett.* **209**, 474 (1993)
52. M.T.D.N. Varella, C. Winstead, V. McKoy, M. Kitajima, H. Tanaka, *Phys. Rev. A: At. Mol. Opt. Phys.* **65**, 022702 (2002)
53. R. Kadokura, A. Loreti, A. Kover, A. Faure, J. Tennyson, G. Laricchia, *Phys. Rev. Lett.* **123**, 033401 (2019)
54. R. Zhang, A. Faure, J. Tennyson, *Phys. Scr.* **80**, 015301 (2009)
55. G.P. Karwasz, R.S. Brusa, L. Del Longo, A. Zecca, *Phys. Rev. A: At. Mol. Opt. Phys.* **61**, 024701 (2000)
56. A. Zecca, G. Karwasz, R.S. Brusa, C. Szmytkowski, *J. Phys. B: At., Mol. Opt. Phys.* **24**, 2747 (1991)
57. G. Garcia, F. Manero, *Phys. Rev. A: At. Mol. Opt. Phys.* **57**, 1069 (1998)
58. C. Makochekanwa, A. Bankovic, W. Tattersall, A. Jones, P. Caradonna, D.S. Slaughter, K. Nixon, M.J. Brunger, Z. Petrovic, J. Sullivan, S.J. Buckman, *New J. Phys.* **11**, 103036 (2009)
59. M. Allan, *J. Phys. B: At., Mol. Opt. Phys.* **38**, 1679 (2005)
60. H. Tanaka, M. Kubo, N. Onodera, A. Suzuki, *J. Phys. B: At., Mol. Opt. Phys.* **16**, 2861 (1983)
61. T.W. Shyn, *J. Phys. B: At., Mol. Opt. Phys.* **24**, 5169 (1991)
62. C.T. Bundschu, J.C. Gibson, R.J. Gulley, M.J. Brunger, S.J. Buckman, N. Sanna, F.A. Gianturco, *J. Phys. B: At., Mol. Opt. Phys.* **30**, 2239 (1997)
63. J.P. Marler, G.F. Gribakin, C.M. Surko, *Nucl. Instrum. Methods Phys. Res., Sect. B* **247**, 87 (2006)
64. V. Laporta, C.M. Cassidy, J. Tennyson, R. Celiberto, *Plasma Sources Sci. Technol.* **21**, 045005 (2012)
65. V. Laporta, D.A. Little, R. Celiberto, J. Tennyson, *Plasma Sources Sci. Technol.* **23**, 065002 (2014)
66. G.P. Karwasz, T. Wróblewski, R.S. Brusa, E. Illenberger, *Jpn. J. Appl. Phys.* **45**, 8192 (2006)
67. J.R. Hamilton, J. Tennyson, S. Huang, M.J. Kushner, *Plasma Sources Sci. Technol.* **26**, 065010 (2017)
68. L. Boesten, Y. Tachibana, Y. Nakano, T. Shinohara, H. Tanaka, M. Dillon, *J. Phys. B: At., Mol. Opt. Phys.* **29**, 5475 (1996)
69. C. Szmytkowski, A. Domaracka, P. Możejko, E. Ptasieńska-Denga, L. Klosowski, M. Piotrowicz, G. Kasperski, *Phys. Rev.* **70**, 032707 (2004)
70. W.F. Chang, G. Cooper, C.E. Brion, *Chem. Phys.* **170**, 111 (1993)
71. X. Xu, L.-Q. Xu, T. Xiong, T. Chen, Y.-W. Liu, L.-F. Zhu, *J. Chem. Phys.* **148**, 044311 (2018)
72. H. Kawahara, D. Suzuki, H. Kato, M. Hoshino, H. Tanaka, O. Ingólfsson, L. Campbell, M.J. Brunger, *J. Chem. Phys.* **131** (2009)
73. S. Dupljanin, J. de Urquijo, O. Šašić, E. Basurto, A.M. Juárez, J.L. Hernández-Ávila, S. Dujko, Z.L. Petrović, *Plasma Sources Sci. Technol.* **19**, 025005 (2010)
74. R.S. Schappe, R.J. Edgell, E. Urban, *Phys. Rev. A: At. Mol. Opt. Phys.* **65**, 042701 (2002)
75. H.C. Straub, P. Renault, B.G. Lindsay, K.A. Smith, R.F. Stebbings, *Phys. Rev. A: At. Mol. Opt. Phys.* **52**, 1115 (1995)
76. B.G. Lindsay, M.A. Mangan, 5.1 Ionization: Datasheet from Landolt-Börnstein – Group I elementary particles, nuclei and atoms, in *Volume 17C: Interactions of Photons and Electrons with Molecules*, edited by Y. Itikawa (Springer-Verlag, Berlin, Heidelberg, 2003)
77. M.D. Ward, S.J. King, S.D. Price, *J. Chem. Phys.* **134**, 024308 (2011)
78. J. Tennyson, D.B. Brown, J.J. Munro, I. Rozum, H.N. Varambhia, N. Vinci, *Phys. Conf. Ser.* **86**, 012001 (2007)
79. J.M. Carr, P.G. Galiatsatos, J.D. Gorfinkiel, A.G. Harvey, M.A. Lysaght, D. Madden, Z. Masin, M. Plummer, J. Tennyson, *Euro. J. Phys. D* **66**, 58 (2012)
80. D. Thirumalai, K. Onda, D.G. Truhlar, *J. Chem. Phys.* **74**, 526 (1981)
81. D. Gupta, R. Nagma, M. Vinodkumar, B. Antony, *J. Electron Spectrosc. Relat. Phenom.* **191**, 71 (2013)
82. S. Motlagh, J.H. Moore, *J. Chem. Phys.* **109**, 432 (1998)
83. L.R. LeClair, J.W. McConkey, *J. Chem. Phys.* **99**, 4566 (1993)

84. J.W. McConkey, C.P. Malone, P.V. Johnson, C. Winstead, V. McKoy, I. Kanik, *Phys. Rep.* **466**, 1 (2008)
85. O. Šašić, G. Malović, A. Strinić, Ž. Nikitović, Z.L. Petrović, *New J. Phys.* **6**, 74 (2004)
86. H.A. van Sprang, G.R. Mohlmann, F.J. de Heer, *Chem. Phys.* **33**, 6 (1978)
87. J. Fedor, XX Intern. Workshop Low-Energy Positron and Positronium Physics, in *XXI Intern. Symp. Electron-Molecule Collisions and Swarms, 18–20 July, 2019, Belgrade, Serbia* (2019) and private information
88. C.E. Melton, *J. Chem. Phys.* **57**, 4218 (1972)
89. M. Vinodkumar, M. Barot, *J. Chem. Phys.* **137**, 074311 (2012)
90. C. Winstead, V. McKoy, *Phys. Rev. A* **57**, 3589 (1998)
91. L.A. Morgan, C.J. Gillan, J. Tennyson, X. Chen, *J. Phys. B* **30**, 4087 (1997)
92. M.H.F. Bettega, C. Winstead, V. McKoy, *Phys. Rev. A: At. Mol. Opt. Phys.* **74**, 022711 (2006)
93. B.K. Sarpal, K. Pfingst, B.M. Nestmann, S.D. Peyerimhoff, *J. Phys. B: At., Mol. Opt. Phys.* **29**, 857 (1996)
94. C. Szmytkowski, G. Karwasz, K. Maciag, *Chem. Phys. Lett.* **107**, 481 (1984)
95. Z. Masin, J. Benda, J.D. Gorfinkiel, A.G. Harvey, J. Tennyson, *Comput. Phys. Commun.* **249**, 107092 (2009)
96. B. Cooper, M. Tudorovskaya, S. Mohr, A. O'Hare, M. Hanicinec, A. Dzarasova, J.D. Gorfinkiel, J. Benda, Z. Masin, A. Al-Refaie, P.J. Knowles, J. Tennyson, *Atoms* **7**, 97 (2019)
97. G. Karwasz, K. Fedus, *Fusion Sci. Technol.* **63**, 338 (2013).
98. W.M. Ariyasinghe, T. Wijeratne, P. Palihawadana, *Nucl. Instrum. Methods Phys. Res., Sect. B* **217**, 389 (2004)
99. R. Ćuric, P. Carsky, M. Allan, *J. Phys. B: At., Mol. Opt. Phys.* **41**, 115203 (2008)
100. S.C. Althorpe, F.A. Gianturco, N. Sanna, *J. Phys. B: At. Mol. Opt. Phys.* **28**, 4165 (1995)
101. M. Brunger, S.J. Buckman, M. T. Elford, 6.4. Excitation cross sections: Datasheet from Landolt-Börnstein – Group I elementary particles, nuclei and atoms, in *Volume 17C: Interactions of Photons and Electrons with Molecules*, edited by Y. Itikawa (Springer-Verlag, Berlin, Heidelberg, 2003)
102. D.M. Bishop, L.M. Cheung, *J. Phys. Chem. Ref. Data* **11**, 119 (1982)
103. B. Goswami, R. Naghma, B. Antony, *Phys. Rev. A: At. Mol. Opt. Phys.* **88**, 032707 (2013)
104. W.F. Chang, G. Cooper, C.E. Brion, *Chem. Phys.* **180**, 77 (1994)
105. B. Marinković, R. Panajotović, Z. Pesić, D.M. Filipović, Z. Felfli, A.Z. Msezane, *J. Phys. B: At., Mol. Opt. Phys.* **32**, 1949 (1999)
106. G.P. Karwasz, P. Mozejko, M.Y. Song, *Int. J. Mass Spectrom.* **365–366**, 232 (2014)