Eur. Phys. J. D (2013)
DOI: 10.1140/epjd/e2012-30691-1

THE EUROPEAN PHYSICAL JOURNAL D

Regular Article

Electron impact ionization cross sections of beryllium and beryllium hydrides

Thana Maihom[1,2], Ivan Sukuba[3], Ratko Janev[4], Kurt Becker[5], Tilmann Märk[1], Alexander Kaiser[1], Jumras Limtrakul[2], Jan Urban[3], Pavel Mach[3], and Michael Probst[1,a]

[1] Institute of Ion Physics and Applied Physics, University of Innsbruck, Innsbruck, Austria
[2] Chemistry Department and Center for Advanced Studies in Nanotechnology and Its Applications in Chemical, Food and Agricultural Industries, Kasetsart University, 10900 Bangkok, Thailand
[3] Department of Nuclear Physics and Biophysics, FMFI UK, Mlynská dolina F1, 84248 Bratislava, Slovakia
[4] Institute of Energy and Climate Research-Plasma Physics, Forschungszentrum Jülich GmbH, Association EURATOM-FZJ, Trilateral Euregio Cluster, 52425 Jülich, Germany
[5] Department of Applied Physics, Polytechnic Institute of New York University, Brooklyn, 11201 NY, USA

Received 15 November 2012 / Received in final form 4 December 2012
Published online (Inserted Later) –

Abstract. We report calculated electron impact ionization cross sections (EICSs) for beryllium (Be) and some of its hydrides from the ionization threshold to 1 keV using the Deutsch-Märk (DM) and the Binary-Encounter-Bethe (BEB) formalisms. The positions of the maxima of the DM and BEB cross sections are very close in each case while the DM cross section values at the maxima are consistently higher. Our calculations for Be are in qualitative agreement with results from earlier calculations (convergent close-coupling, R matrix, distorted-wave and plane-wave Born approximation) in the low energy region. For the various beryllium hydrides, we know of no other available data. The maximum cross section values for the various compounds range from 4.0×10^{-16} to 9.4×10^{-16} cm^2 at energies of 44 to 56 eV for the DM cross sections and 3.0×10^{-16} to 5.4×10^{-16} cm^2 at energies of 40.5 to 60 eV for the BEB cross sections.

1 Introduction

Beryllium (Be) is one of the materials that will be directly exposed to plasma components in the international thermonuclear experimental reactor (ITER) [1]. Erosion of the Be walls will occur when it is in contact with the hot plasma containing hydrogen and its isotopes [2,3]. This leads to the formation of gas-phase Be in various charge states and of Be hydrides, i.e. BeH_2. The presence of these species in the fusion edge and divertor plasmas influences them, for example, due to electron collision processes, which are quantified by their respective EICS and other electron impact cross sections. There is not much cross section information available concerning Be and its hydrides up to now. In this work, we aim to partially close this gap by reporting calculated EICSs. EICS data are, of course, also important in a variety of other applications such as low-temperature processing plasma, gas discharges, astrophysics and chemical analysis [4].

During the past decades, a number of semi-empirical methods that use quantum-mechanically calculated input information have been developed to calculate absolute EICSs for various molecules. Their accuracy is normally similar to that of experimental data. Among those, the most widely used methods are the binary-encounter-bethe (BEB) theory of Kim et al. [5,6] and the Deutsch-Märk (DM) formalism [7]. These methods have been successfully applied to calculate atoms, molecules, clusters, ions, and radicals as well [8].

In this paper, we present results of calculations of the EICS of Be and its hydrides BeH, BeH_2, Be_2H_2 and Be_2H_4 using the Deutsch-Märk (DM) and the Binary-Encounter-Bethe (BEB) formalisms. To our knowledge, no cross sections for the ionization of Be or Be-containing molecules has been published with these methods before. It should be noted that in reference [9] cross sections for the formation of Be^{2+}, Be^{3+} and Be^{4+} are given, but not for Be^+.

2 Background

2.1 DM method

The DM formalism was originally developed as an easy-to-use semi-empirical approach for the calculation of EICSs for atoms in their electronic ground-state from threshold to about 100 eV as input for plasma modeling codes [7]. The DM formalism in its most recent variant [8,10] expresses the total single electron-impact ionization cross

[a] e-mail: michael.probst@uibk.ac.at

section σ of an atom as:

$$\sigma(u) = \sum_{n,l} g_{nl}\pi r_{nl}^2 \xi_{nl} b_{nl}^{(q)}(u)[\ln(c_{nl}u)/u] \quad (1)$$

where r_{nl} is the radius of maximum radial density of the atomic subshell characterized by quantum numbers n and l (as listed in column 1 in the tables of Desclaux [11]) and ξ_{nl} is the number of electrons in that sub-shell. The sum extends over all atomic sub-shells labelled by n and l. The g_{nl} are weighting factors, which were originally determined from a fitting procedure [12,13] using reliable experimental cross section data for a few selected atoms, where the accuracy of the reported rate is in the range from 7−15%. The "reduced energy" u is given by $u = E/E_{nl}$, where E refers to the incident energy of the electrons and E_{nl} is the ionization energy in the (n, l) subshell. The energy-dependent quantities $b_{nl}^{(q)}(u)$ were introduced in an effort to merge the high-energy region of the ionization cross section, which follows the Born-Bethe approximation [14] with the DM formula of the cross sections in the regime of low impact energies. The function $b_{nl}^{(q)}(u)$ in equation (1) has the explicit form:

$$b_{nl}^{(q)}(u) = \frac{A_1 - A_2}{1 + (u/A_3)^p} + A_2, \quad (2)$$

where the four quantities A_1, A_2, A_3, and p are constants that were determined, together with c_{nl}, from reliable measured cross sections for the various values of n and l [8]. The superscript "q" refers to the number of electrons in the (n, l) subshell and allows the possibility to use slightly different functions $b_{nl}^{(q)}(u)$ depending on the number of electrons in a given (n, l) sub-shell. At high impact energies u approaches infinity, the first term in equation (2) goes to zero and $b_{nl}^{(q)}(u)$ becomes a constant ensuring the high-energy behaviour predicted by the Born-Bethe theory [14]. The constant c_{nl} in equation (1) was found to be close to one except for d-electrons.

As discussed in reference [8], the DM formalism was subsequently extended to the calculation of electron-impact ionization of atomic in excited states, molecules and free radicals, atomic and molecular ions, and clusters. For the calculation of the EICS of a molecule, a population analysis [15,16] must be carried out to obtain the weights with which the atomic orbitals of the constituent atoms contribute to each occupied molecular orbital (MO). These weights are obtained from the MO coefficients by correcting them with the overlap matrix due to the nonorthogonality of the basis functions.

In this study, the orbital populations used in the DM formula were derived from ROHF calculations with a small CEP-4G basis set [17], while molecular geometries were optimized with using the QCISD method and the aug-cc-pVTZ basis set [18]. The orbital energies (ionization potentials) were calculated with the outer-valence Green's functions method (OVGF) [19,20] and the same basis set.

2.2 BEB method

The BEB model [5] was derived from the binary-encounter-dipole (BED) model [6] by simplification of the term *df/dE* for the continuum dipole oscillator strengths, which was replaced by a simple form. Thus, a modified form of the Mott cross section together with the asymptotic form of the Bethe theory for electron-impact ionization of an atom was combined into an expression for the cross section of each molecular orbital:

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

where $t = T/B$, $u = U/B$, $S = 4\pi a_0^2 N R^2/B^2$, a_0 is the Bohr radius (0.5292 Å), R is the Rydberg energy (13.6057 eV) and T is the incident electron energy. N, B, and U are the electron occupation number, the binding energy (ionization potential), and the average kinetic energy of the orbital, respectively. In our calculations, both quantities were derived from Hartree-Fock calculations with the aug-cc-pVTZ basis set [18]. The total cross section is, as in the DM method, a sum over the cross section of each MO.

3 Results and discussion

We begin with the Be atom. The calculated OVGF value of the ionization threshold is 9.32 eV, which compares well with experimental data from [21]. There are no reliable experimental ionization cross section data for Be in the literature. However, we can compare the result of the present DM and BEB calculations for the ionization cross section of Be with predictions from convergent close-coupling (CCC), R matrix with pseudostates (RMPS), distorted-wave with electron scattering (DWIS(N-1)) [22] and the plane-wave Born approximation (PWBA) [23] methods as shown in Figure 1. The details of these approaches can be found in the cited literatures. The DM cross section maximum is 3.96×10^{-16} cm^2 at 31 eV, about 25% higher than that of the BEB calculation (3.15×10^{-16} cm^2 at 40.5 eV). At higher impact energies both curves approach each other. The CCC and RMPS calculations have maxima at 20–30 eV of about 50% of the DM maximum and 25% of the BEB maximum. The DWIS(N-1) maximum value lies roughly 25% below the DM value. The DM and PWBA cross section maxima nearly coincide with each other but the PWBA curve falls off more rapidly at larger energies. The scatter in the values of the cross section maximum, in the energetic position of the maximum, and in the energy dependence derived from the various models is perhaps somewhat larger than what one finds for other atoms, but not that uncommon either [24,25].

For BeH and BeH_2, the geometries obtained from the QCISD/aug-cc-pVTZ level of theory are shown in Figures 2a and 2b. The calculated bond Be-H distance is 1.35 Å in BeH and 1.33 Å in BeH_2, respectively, in good agreement with the experimental results of 1.34 and 1.33 Å for BeH and BeH_2, respectively [26–28]. BeH_2 in the

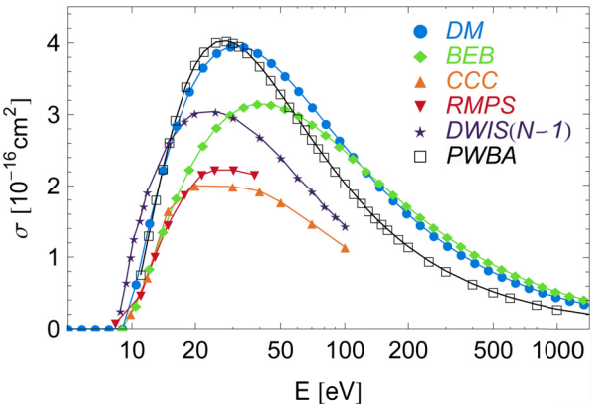

Fig. 1. (Color online) Electron impact ionization cross section of Be: Deutsch-Märk (DM) cross section (circle), binary-encounter-Bethe (BEB) (diamond), CCC (triangle) [20], RMPS (inverted triangle) [20], DWIS(N-1) (star) [23] and PWBA (square) [24,25] calculations.

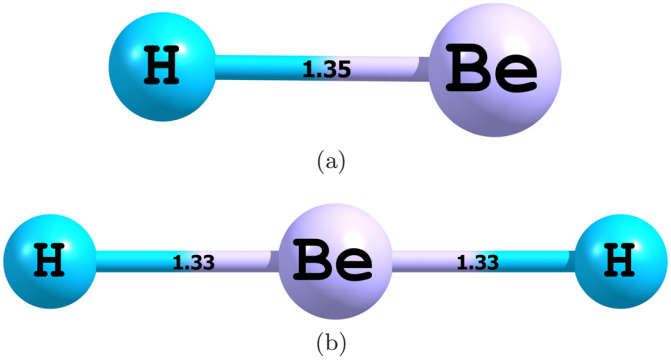

Fig. 2. (Color online) Minimum-energy structures of (a) BeH and (b) BeH_2 from QCISD/aug-cc-pVTZ calculations.

ground state is a linear molecule. The DM and BEB results for the EICS of these molecules are displayed in Figure 3. For BeH, the ionization threshold is 8.28 eV, close to its experimental ionization potential [29]. For BeH_2, the threshold is at 11.93 eV, which is in agreement with former CI calculations [30]. To the best our knowledge, no experimental and calculated EICS data have been published for BeH and BeH_2. The DM cross section maxima for BeH and BeH_2 are 4.0×10^{-16} cm^2 at 44 eV and 4.8×10^{-16} cm^2 at 50 eV, respectively. The BEB cross section maxima are 3.0×10^{-16} cm^2 at 50 eV and 2.9×10^{-16} cm^2 at 58 eV, for BeH and BeH_2, respectively. It can be seen that the DM cross sections are about 25% larger than the BEB values for BeH and about 40% for BeH_2. Inspecting the MO contributions one sees that that these differences appear in each of the relevant MOs. For molecules, 25% to 50% discrepancies between the results of different calculations, as well as similar discrepancies between calculated and experimentally determined ionization cross sections are not unusual [5,8,13].

BeH and BeH_2 are the smallest units in a well-known series of polymers [31]. Energetics and properties obtained at the QCISD/aug-cc-pVTZ level of theory are given in

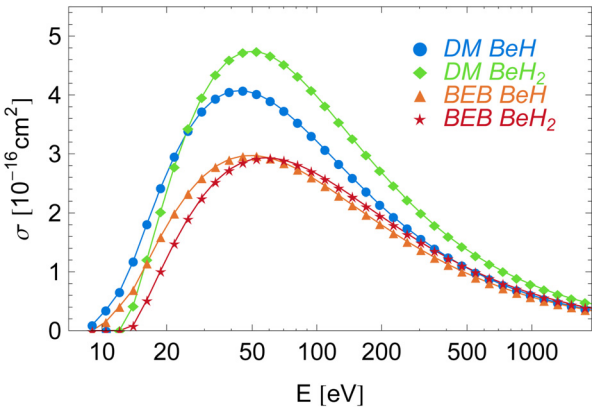

Fig. 3. (Color online) Electron-impact ionization cross section of BeH and BeH_2 from the DM and BEB methods.

Table 1. Geometrical parameters and relative energies of the Be_xH_y species obtained at the QCISD/aug-cc-pVTZ level of theory.

Parameter	BeH	BeH_2	Be_2H_2	Be_2H_4
distance (Å)				
Be−H	1.35	1.33	–	–
Be−Be	–	–	2.09	2.00
Be−H_{end}	–	–	1.34	1.33
Be−H_{bridge}	–	–	–	1.47
angle (°)				
∠ H−Be−H	–	180.0	–	–
∠ H−Be−Be	–	–	180.0	179.8
∠ H_{end}−Be−H_{bridge}	–	–	–	132.8
∠ Be−H_{bridge}−Be	–	–	–	85.9
Energy (eV)*	0	0	−1.59	−0.71

* According to the equation: $\Delta E = (E((Be_xH_y)_n) - nE(Be_xH_y))/n$.

Table 1 along with those of Be_2H_2 and Be_2H_4. We also calculated the cross sections for Be_2H_2 and Be_2H_4 (Fig. 4). Under fusion conditions, these species will have low concentrations in the plasma, since the equilibrium at high temperatures and low pressures is shifted to the side of the monomers. While Be_2H_2 is a linear molecule in its minimum-energy configuration, the two H additional atoms in Be_2H_4 bridge the two Be atoms. The distances of Be-H are 1.47 and 1.33 Å for bridge and end, respectively. The angles of Be-H-Be and H-Be-H are 85.9° and 103.8°, respectively. Figure 5 shows the results of the DM and BEB calculations of the ionization cross section for these molecules. The ionization thresholds for Be_2H_2 and Be_2H_4 are estimated to be 9.61 and 11.65 eV, respectively. The DM cross section maxima are at 8.6×10^{-16} cm^2 at 46 eV and 9.4×10^{-16} cm^2 at 56 eV for Be_2H_2 and Be_2H_4, respectively, while the ones from BEB calculations are again about 40% lower for the two species (5.4×10^{-16} cm^2 at 52.5 eV and 5.3×10^{-16} cm^2 at 60 eV for Be_2H_2 and Be_2H_4, respectively). All maxima are around two times higher than the maxima for the monomers BeH and BeH_2.

Table 2. The four fit parameters in equation (3). Using these values, the cross section σ is obtained in units of 10^{-16} cm^2.

	Parameter	Be	BeH	BeH_2	Be_2H_2	Be_2H_4
DM	a_1	70.3260	102.6331	146.1137	216.6041	320.1019
	a_2	1.2341	2.6155	1.7365	2.5258	2.1647
	a_3	1.7644	1.4374	1.2759	1.8284	1.2286
	a_4	−0.7628	−0.4850	−0.4094	−0.3356	−0.3330
BEB	a_1	116.2331	116.8453	140.9422	229.2566	261.1648
	a_2	1.4996	3.3456	2.3253	2.9241	2.5178
	a_3	0.0295	0.2820	0.2744	0.2802	0.2700
	a_4	0.5720	1.5601	1.0397	1.3934	0.9802

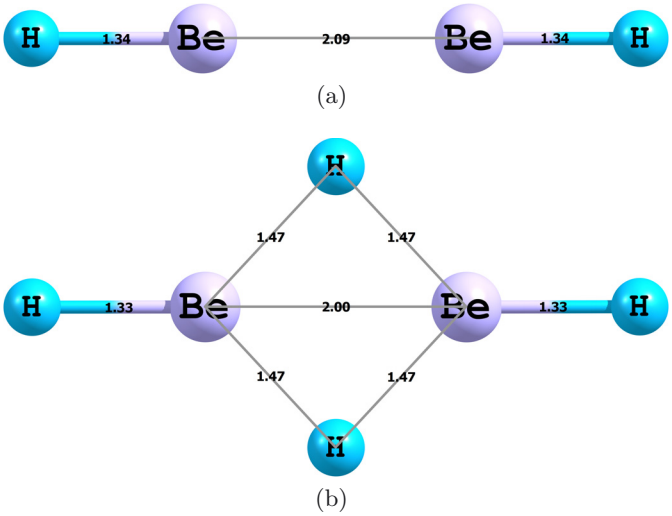

Fig. 4. (Color online) Minimum-energy structures of (a) Be_2H_2 and (b) Be_2H_4 from QCISD/aug-cc-pVTZ calculations.

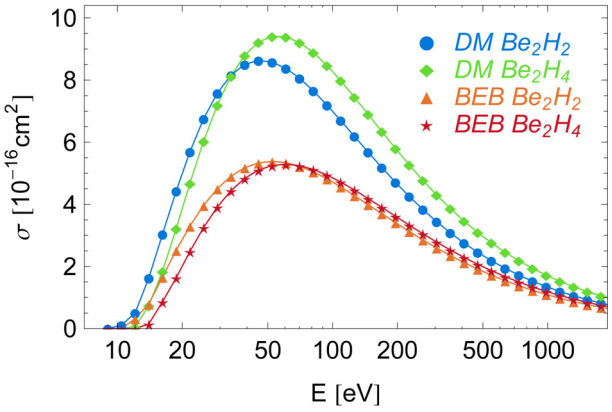

Fig. 5. (Color online) Electron-impact ionization cross sections of Be_2H_2 and Be_2H_4 from the DM and BEB methods.

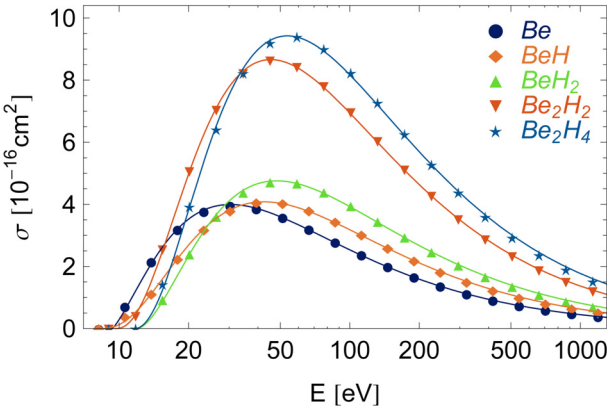

Fig. 6. (Color online) Cross sections (solid lines) obtained from fitting the DM values (symbols) to equation (3).

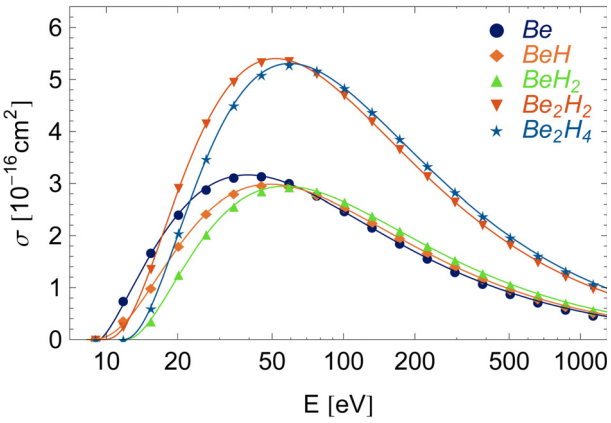

Fig. 7. (Color online) Cross sections (solid lines) obtained from fitting the BEB values (symbols) to equation (3).

Such a trend was also found, for example, for cross section calculations of hydrocarbons with the BEB model [5] and the DM formalism [8,13] and reflect the fact that these are additive models.

Finally, we investigated how well a fit formula of the type

$$\sigma(E) = (a_1/E)\,[1-(E_t/E)]^{a_2}\,[\ln(E/E_t)+a_3+a_4(E_t/E)], \quad (3)$$

reproduces the cross sections. σ is expressed in 10^{-16} cm^2, E and the threshold energy E_t in eV. The parameters a_1 to a_4 are fitted. In the fitting procedure, logarithmic weighting was used so that the low-energy features are not suppressed by the high-energy tails. The results are shown in Figures 6 and 7 for DM and BEB methods, respectively. It can be seen that expression (3) gives an excellent fit to all cross section data. The numerical values of the fitting parameters are given in Table 2.

4 Conclusions

We applied the Deutsch-Märk (DM) and binary-encounter-Bethe (BEB) formalisms to calculate the absolute electron impact ionization cross-sections for Be and some of its hydrides in the ground state from ionization threshold to 1 keV. The cross section for the Be atom from both methods is in the range of former results from CCC, RMPS, DWIS(N-1) and PWBA calculations. For the Be_xH_y species, the DM cross section maxima are at 4.0, 4.8, 8.6 and 9.4 $cm^2 \times 10^{-16}$ for BeH, BeH_2, Be_2H_2 and Be_2H_4, respectively, in the energy range of 44–56 eV. These values are about 25% higher for BeH and BeH_2 and 40% higher for Be_2H_2 and Be_2H_4 than the corresponding BEB maxima. This discrepancy between the results of the two approaches is not uncommon in the case of molecules and is considered reasonable, see e.g. [8,13]. In a subsequent work, we plan to calculate EICSs for excited and ionic states of these hydrides.

This work was supported by the Austrian Ministry of Science BMWF as part of the university infrastructure program of the scientific computing platform at LFU Innsbruck and by the European Commission under the Contract of Association between EURATOM and the Austrian Academy of Sciences and was carried out within the framework of the European Fusion Development Agreement. The views and opinions expressed herein do not necessarily reflect those of the European Commission. A.K. is funded by the Austrian Science Fund (FWF) DK+ project Computational Interdisciplinary Modeling, W1227-N16. J.L. and T.M. acknowledge support by grants from the National Science and Technology Development Agency ("NANOTEC Center for the Design of Nanoscale Materials for Green Nanotechnology" and "NSTDA Chair Professor"), the Commission on Higher Education, Ministry of Education "National Research University of Thailand" and the program "Strategic Scholarships for a Frontier Research Network for joint Thai Ph.D. Programs" to T.M.

References

1. G. Federici, Phys. Scr. T **124**, 1 (2006)
2. R. Doerner, M.J. Baldwin, D. Buchenauer, G. De Temmerman, D. Nishijima, J. Nucl. Mater. **390**, 681 (2009)
3. C. Björkas, K. Vörtler, K. Nordlund, D. Nishijima, R. Doerner, New J. Phys. **11**, 123017 (2009)
4. T.D. Märk, G.H. Dunn, *Electron Impact Ionization* (Springer, Wien, 1985)
5. Y.K. Kim, M.A. Ali, M.E. Rudd, J. Res. NIST **102**, 693 (1997)
6. Y.K. Kim, M.E. Rudd, Phys. Rev. A **50**, 3954 (1994)
7. H. Deutsch, T.D. Märk, Int. J. Mass Spectrom. Ion Proc. **79**, R1 (1987)
8. H. Deutsch, K. Becker, M. Probst, T.D. Märk, Adv. At. Mol. Opt. Phys. **57**, 87 (2009)
9. H. Deutsch, K. Becker, G. Senn, S. Matt, T.D. Märk, Int. J. Mass Spectrom. **192**, 1 (1999)
10. H. Deutsch, P. Scheier, K. Becker, T.D. Märk, Int. J. Mass Spectrom. **233**, 13 (2004)
11. J.P. Desclaux, At. Data Nucl. Data Tables **12**, 325 (1973)
12. D. Margreiter, H. Deutsch, T.D. Märk, Int. J. Mass Spectrom. Ion Proc. **139**, 127 (1994)
13. H. Deutsch, K. Becker, S. Matt, T.D. Märk, Int. J. Mass Spectrom. Ion Proc. **197**, 37 (2000)
14. H. Bethe, Ann. Phys. **5**, 325 (1930)
15. R.S. Mulliken, J. Chem. Phys. **23**, 1833 (1955)
16. R. Tang, J. Callaway, J. Chem. Phys. **84**, 6854 (1986)
17. W. Stevens, H. Basch, J. Krauss, J. Chem. Phys. **81**, 6026 (1984)
18. R.A. Kendall, T.H. Dunning Jr., R.J. Harrison, J. Chem. Phys. **96**, 6796 (1992)
19. W. von Niessen, J. Schirmer, L.S. Cederbaum, Comput. Phys. Rep. **1**, 57 (1984)
20. V.G. Zakrzewski, J.V. Ortiz, J. Phys. Chem. **100**, 13979 (1996)
21. A.E. Kramida, W.C. Martin, J. Phys. Chem. Ref. Data **26**, 1185 (1997)
22. J. Colgan, S.D. Loch, M.S. Pindzola, Phys. Rev. A **68**, 032712 (2003)
23. P.L. Bartlett, A.T. Stelbovics, At. Data Nucl. Data Tables **86**, 235 (2004)
24. H. Deutsch, P. Scheier, S. Matt-Leubner, K. Becker, T.D. Märk, Int. J. Mass Spectrom. **243**, 215 (2005)
25. H. Deutsch, P. Scheier, S. Matt-Leubner, K. Becker, T.D. Märk, Int. J. Mass Spectrom. **246**, 113 (2005), erratum
26. R.J. Le Roy, D.R.T. Appadoo, R. Colin, P.F. Bernath, J. Mol. Spectrosc. **236**, 178 (2006)
27. P.F. Bernath, A. Shayesteh, K. Tereszchuk, R. Colin, Science **297**, 1323 (2002)
28. A. Shayesteh, K. Tereszchuk, P.F. Bernath, R. Colin, J. Chem. Phys. **118**, 3622 (2003)
29. R. Colin, D. DeGreef, P. Geothals, G. Verhagen, Chem. Phys. Lett. **25**, 70 (1974)
30. R. Cambi, G. Ciullo, A. Sgamellotti, F. Tarantelli, Chem. Phys. Lett. **83**, 320 (1981)
31. X. Wang, L. Andrews, Inorg. Chem. **44**, 610 (2005)