Available online at www.sciencedirect.com
SCIENCE DIRECT®
Nuclear Instruments and Methods in Physics Research B 247 (2006) 87–91
NIM B
Beam Interactions with Materials & Atoms
www.elsevier.com/locate/nimb

Comparison of positron-impact vibrational excitation cross sections with the Born-dipole model

J.P. Marler [a], G.F. Gribakin [b], C.M. Surko [a,*]

[a] Department of Physics, University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093-0319, USA
[b] Department of Applied Mathematics and Theoretical Physics, Queen's University Belfast, Belfast BT7 1NN, Northern Ireland, UK

Available online 15 March 2006

Abstract

The development of cold trap-based positron beams and new scattering techniques has recently enabled the first measurements of state-resolved positron-impact vibrational excitation cross sections. These measurements revealed a number of features worth further consideration, such as relatively sharp increases near threshold. This paper describes a comparison of the magnitudes and shapes of these cross sections with the predictions of the Born-dipole model. Agreement of the magnitudes of the cross sections varies widely, ranging from reasonable to excellent agreement for CO_2 and CF_4 to poor agreement for CO and CH_4. In contrast, the energy dependence of these cross sections in all these cases is close to that predicted by the Born model.
© 2006 Elsevier B.V. All rights reserved.

PACS: 34.85.+x; 34.80.Gs; 34.50.Ez

Keywords: Positron scattering; Vibrational excitation

1. Introduction and overview

The advent of trap-based positron beams and a new scattering technique exploiting the properties of positron orbits in a magnetic field have permitted the first measurements of state-resolved integral electronic and vibrational excitation cross sections for the case of positron-impact [1,2]. Vibrational excitation of a number of molecules has now been studied including CF_4, CO, H_2, CH_4 and CO_2. A study of vibrational excitation of the ν_3 asymmetric stretch mode in CF_4 by both positron- and electron-impact was recently conducted in the same apparatus to minimize systematic effects [3]. The results show that the CF_4 vibrational cross section is the largest of any positron-impact vibrational-excitation cross section measured to date. It is also the first known example where the cross sections for positron- and electron-impact are virtually identical (i.e. both in magnitude and shape). This strong similarity motivated comparison of these cross sections with the Born-dipole model [4,5], since in the context of this model, the cross sections for positron-impact and electron-impact excitation are identical. Qualitatively, the Born-dipole model (BDM) is applicable when the long-range electrostatic coupling of the charged projectile to the molecular transition dipole is the dominant vibrational excitation mechanism. In the case of CF_4, this is plausible, since there is a large amount of electron-charge transfer from the carbon to the fluorine atoms, resulting in a large dipole excitation amplitude for the asymmetric stretch mode.

These observations led us to consider further comparisons of the existing measurements with the predictions of the Born-dipole model. Comparisons are presented here for CO, CH_4 and CO_2 [2,6]. It is found that none of the five infrared-active modes examined here are described by the BDM as accurately as the ν_3 mode of CF_4. The cross sections predicted by the BDM for the other modes studied account for varying fractions of the measured values,

* Corresponding author. Tel.: +1 858 534 6880; fax: +1 858 534 6574.
E-mail addresses: joanmarler@gmail.com (J.P. Marler), g.gribakin@qub.ac.uk (G.F. Gribakin), csurko@ucsd.edu (C.M. Surko).

0168-583X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.nimb.2006.01.042

ranging from about 60% for the ν_2 mode of CO_2 to less than 20% for the sum of the $\nu_3 + \nu_1$ modes of CH_4. However the energy dependence of all cross sections is quite similar to the Born-model prediction. In contrast, the measured cross section for H_2 (i.e. a case where the dipole coupling is zero due to symmetry) has a qualitatively different energy dependence. Other trends in the data are discussed, including comparisons with measured electron-impact cross sections where available.

The experimental measurements discussed here were made with a cold, trap-based positron beam [7] with an energy resolution of 25 meV, FWHM. Scattering was studied using a method that exploits the orbits of the positrons in a strong magnetic field [1,2,8]. This technique has proven to be particularly useful in measuring absolute integral inelastic excitation cross sections (i.e. without the need for normalization to other data). The experimental technique is described in detail in [8], and as applied specifically to measurement of vibrational excitation cross sections, it is also described in [1,2].

2. Born-dipole approximation

While the Born approximation is typically regarded as valid only at high energies, another region of applicability is the one considered here. Due to the low energy of molecular vibrational excitations and long-range nature of the charge-dipole coupling, the amplitude of vibrational excitation of an infrared-active mode is dominated by large projectile-target distances. In this case, the projectile wavefunction is only weakly perturbed by the interaction with the target. In addition, for projectile energies somewhat higher than threshold, many partial waves with large angular momenta contribute to the cross section (classically, large impact parameters are important). These partial-wave components of the projectile wavefunction are close to the corresponding components of a plane wave.

In the BDM, the differential and integral cross sections of the vibrational excitation of mode n of a molecule are given by [4,5],

$$\frac{d\sigma}{d\Omega} = \frac{4k'}{3k}\frac{M_n^d}{k^2 + k'^2 - 2kk'\cos\theta}, \quad (1)$$

$$\sigma = \frac{8\pi}{3k^2} M_n^d \ln[(k+k')/(k-k')], \quad (2)$$

where all quantities are in atomic units; k and $k' = \sqrt{k^2 - 2\omega_n}$ are the initial and final positron (electron) momenta, ω_n is the energy of the mode and M_n^d is the dipole transition strength, including the mode degeneracy factor. The absolute values of the transition strengths, M_n^d, and hence the effective transition dipole matrix elements, $D_n = \sqrt{M_n^d}$, for many molecules and modes have been determined by infrared absorption measurements [9,5]. Eqs. (1) and (2) provide absolute predictions of the differential and integral cross sections for vibrational excitation by positron- or electron-impact.

A comparison of the BDM with measured cross sections for both positron- and electron-impact excitation of the ν_3 vibrational mode of CF_4 has recently been presented in [3]. As shown in Fig. 1, both the positron and electron data are in good, absolute agreement with the BDM predictions. The measurements shown in Fig. 1 for both positrons and electrons are the first direct, integral, state resolved cross section measurements for the ν_3 mode of CF_4. Other measurements of the integral cross section for electrons using swarm techniques [10,11] and a combination of differential cross section measurements and the BDM [12] are discussed in [3].

In CF_4, there is extensive electron charge-transfer between the carbon and fluorine atoms, resulting in strong dipole coupling to the asymmetric stretch mode. For molecules with smaller transition dipole amplitudes, the long-range dipole coupling will give a smaller contribution to the excitation amplitude. One can expect that, in this case, short-range effects not described by the BDM may become relatively more important, leading to deviations of the cross sections from the predictions of Eqs. (1) and (2).

In Figs. 2–5, we compare the predictions of the BDM with positron-impact data for the other molecules and modes studied to date. Note that in Fig. 4, the data correspond to the pairs of modes, $\nu_1 + \nu_3$ and $\nu_2 + \nu_4$, since the experimental resolution was insufficient to resolve the individual members of each pair. In this case, one mode in each pair (i.e. the ν_3 and ν_4 modes) is infrared active. The other two modes (ν_1 and ν_2) are not infrared active, resulting in an absence of dipole coupling.

To quantify the degree of disagreement between the BDM and the measurements and to analyze the energy dependence of the cross sections, we show the BDM predictions scaled to fit the experimental data. In particular, we assume that $\sigma_{exp} = f_{BD}\sigma_B$, where σ_B is the Born-dipole

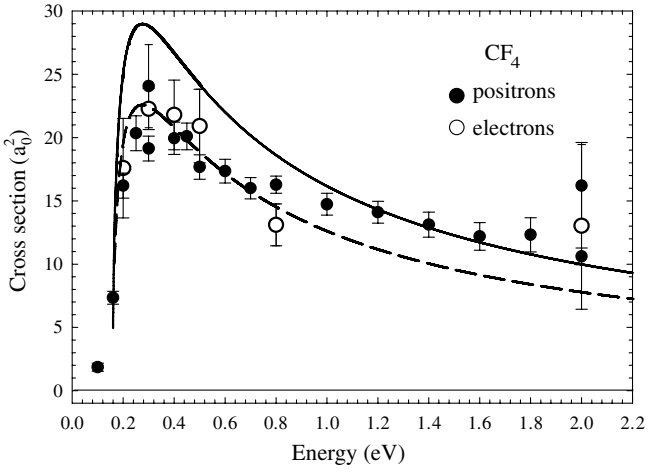

Fig. 1. Comparison of the experimental results for positron-impact excitation of the ν_3 mode of CF_4 [3] with: (—) the Born-dipole model [5], and (--) the Born-dipole model with the magnitude adjusted to fit the data. Also shown for comparison are the electron-impact data (○) taken using the same experimental apparatus [3].

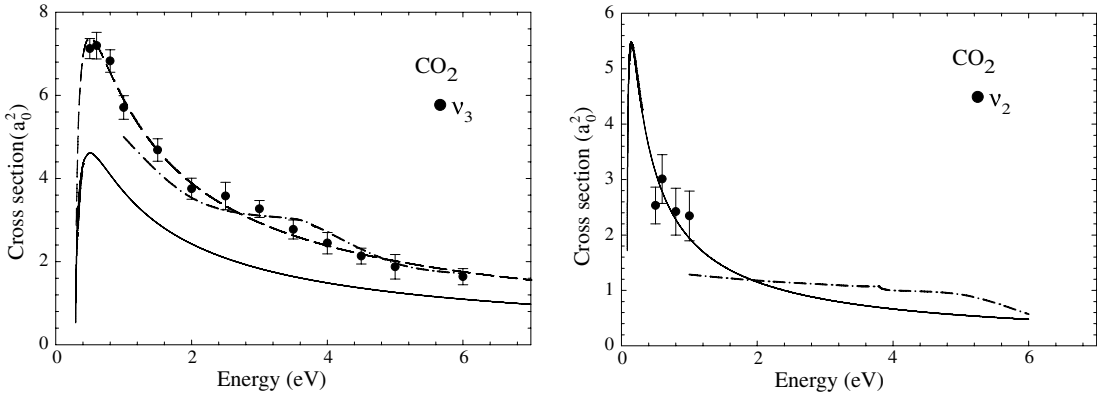

Fig. 2. Comparison of the experimental results for positron-impact excitation of the (left) ν_3, and (right) ν_2 vibrational modes of CO_2 [2] with (—) the Born-dipole model [5]; (--) the Born-dipole model with the magnitude adjusted to fit the data; and (–·–) the predictions of Kimura et al. [13]. The Born model can account for about 63% of the measured cross section for the ν_3 mode and all of the cross section for the ν_2 mode. Note that the energy dependence predicted by the BDM for the ν_3 mode agrees well with the measured cross section.

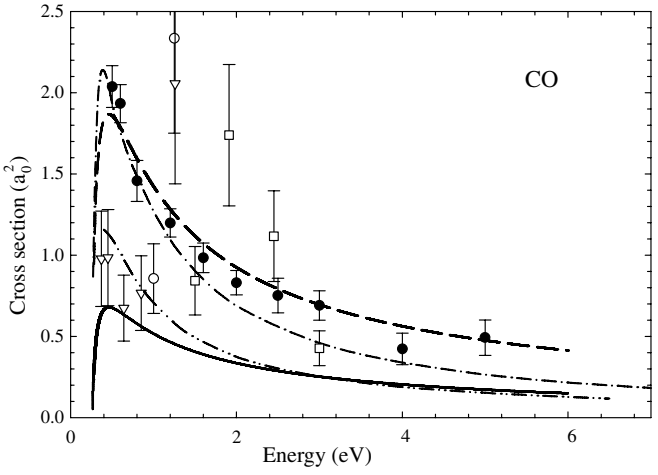

Fig. 3. Comparison of the experimental results for positron-impact excitation of CO [2] with (—) the Born-dipole model [5]; (- -) the Born model with the amplitude adjusted to fit the data; (–·–) the predictions of Gianturco et al. [14]; and (–··–) the predictions of Jain [15]. The Born model can account for about 36% of the measured cross section and fits the shape quite well. Also shown for comparison are the electron-impact data (○, ▽)from [16] and [17]. Above 1.5 eV (i.e. in the region of the $^2\Pi$ resonance) the data of [16] (□) have been multiplied by 0.1.

cross section, σ_{exp} is the measured cross section, and f_{BD} is a fitting constant for each mode or unresolved mode pair. Comparisons of the magnitudes of the predicted and measured spectra are summarized in Table 1. Of all cases studied, CF_4 is the only one where the BDM accounts for all of the measured cross section. In fact, it overestimates the peak cross section by almost 30%. In contrast, the results of Figs. 2–4 show varying and generally lesser degrees of agreement with the Born model. The values of σ_B from the BDM are shown by the solid lines in Figs. 2–4. Table 1 also shows the transition dipole matrix element, D_n, and the values of f_{BD} that yield best fits to the data. With regard to comparisons of the magnitudes of the cross sections, the BDM predictions for CF_4 and CO_2 agree reasonably well with the measurements, especially the low-energy bending mode ν_2 (albeit over a limited range of data), with less good agreement for the other targets studied. Note that after CF_4, CO_2 has the largest vibrational excitation cross section in the Born-dipole approximation, with those of CO and CH_4 smaller by a factor of four or more. In the later two cases, the weakness of the long-range dipole coupling makes other short-range contributions to the amplitude more important. In the case of the $\nu_1 + \nu_3$ modes of CH_4, dipole coupling accounts for only 18% of the measured cross section.

As shown in Fig. 2, the theoretical predictions of [13] for CO_2 are in good agreement with experiment for the ν_3 mode, and those of [14] describe the data for CO quite well (Fig. 3). In contrast, Fig. 4 shows that the theoretical results of [18] for both cross sections in CH_4 fall considerably below the experimental data.

In contrast with the widely varying degrees of agreement between the BDM and the magnitudes of the measured cross sections, the *shapes* of the measured spectra agree fairly well with the Born model for all targets studied except H_2, which is the one case where the dipole coupling is absent. In particular, the Born model prediction captures the general trend of the data that show a sharp rise in the cross section near threshold followed by a monotonic and rather slow decrease at higher energies. The measured cross section for H_2 also rises sharply from threshold (cf. Fig. 5). However, it decreases much faster than the BDM prediction after the maximum. Whether the agreement for the shapes of the cross sections for CO_2, CO, and CH_4 is significant, even when the magnitudes of the BDM predictions are significantly smaller than the measurements, or is merely a coincidence, is presently unclear. In this regard, the H_2 data provide an example of a case where the dependence of the cross section on energy is distinctly different than that predicted by the BDM.

While the sharp rise in the cross section near threshold is seen in the electron-impact data for CF_4, to our knowledge there are no directly measured integral electron-impact vibrational cross sections for the other targets and modes

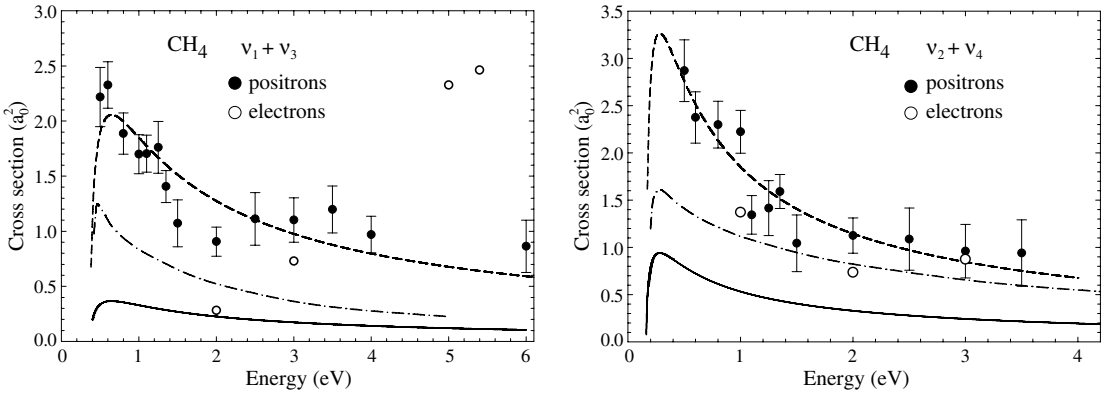

Fig. 4. Experimental results for positron-impact excitation of the unresolved pairs of modes (left) $\nu_1 + \nu_3$, and (right) $\nu_2 + \nu_4$ vibrational modes of CH_4 [6]. Shown for comparison are (—) the Born-dipole model for the infrared-active modes (left) ν_3; and (right) ν_4; (--) the Born model with amplitudes adjusted to fit the data; and (—·) the predictions of [18]. While the Born model can account for only a relatively small fraction of the cross sections, it fits the shapes of the cross sections reasonably well. For comparison, open symbols are electron-impact data from [19].

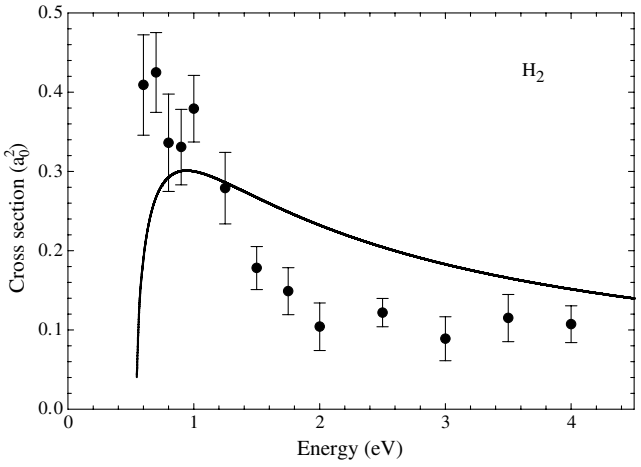

Fig. 5. Experimental results for positron-impact excitation of H_2 from [2]. Note that, in contrast to the data shown for the other molecules studied, the energy dependence of the measured cross section differs markedly from that of the BDM (—). This is expected, since the dipole coupling for H_2 is zero by symmetry.

considered here. Thus, the behavior of the electron-impact cross sections near threshold remains to be determined. In principal, this, and systematic comparisons with the analogous positron cross sections, could be done using the trap-based beam apparatus and an electron source, as was used for the recent study of CF_4 [3].

There are, however, measurements of differential vibrational excitation cross sections (DCS) by electrons for all of the molecules listed in Table 1. In particular, data at ~1 eV and higher energies are available for CF_4 [5], CO_2 [20], CO [16,17] and CH_4 [19]. Thus a comparison of the measured electron-impact DCS with Eq. (1) then allows us to compare the applicability of the BDM for positrons and electrons for the same molecules and modes.

For the ν_3 mode in CF_4, the DCS at 2 eV (i.e. the lowest energy studied) measured at 20°, 50° and 90° are within about 10% of the prediction of the BDM. This agreement is similar to that in [3] for the integral positron and electron cross sections for CF_4. In CO_2, the electron DCS for the ν_2 bending mode is very close to the BDM prediction over the measurement range, $15° < \theta < 105°$, at 0.33 and 1.05 eV [20]. This cross section is strongly forward-peaked, suggesting that the corresponding integral cross section would also be in accord with the BDM. This is in accord with the positron results (cf. Fig. 2, right panel) that show good agreement with the BDM, at least over the limited range for which data is available. The measured electron-impact DCS for the ν_3 (asymmetric stretch) mode in CO_2 is about 30% larger than the BDM at 0.53 eV (evaluated using a

Table 1
Comparison of the Born-dipole model predictions with integral, positron-impact vibrational-excitation cross section measurements

Molecule	Mode number	ω_n (eV)	D_n (a.u.)	σ_{exp} (1 eV) (a_0^2)	σ_B (1 eV) (a_0^2)	f_{BD}^{-1}
CF_4	3	0.159	0.210	15	16.5	1.28
CO_2	3	0.291	0.113	5.8	3.7	0.63
CO_2	2	0.083	0.067	2.4	1.9	1.0
CO	1	0.266	0.042	1.25	0.53	0.36
CH_4	4 [2][a]	0.163 [0.190]	0.039	1.8	0.54	0.29
CH_4	3 [1][a]	0.374 [0.362]	0.037	1.6	0.33	0.18
H_2	1	0.545	0	0.33	n.a.	n.a

Tabulated are the mode frequencies, ω_n, the transition dipole matrix elements D_n from Ref. [9], the experimental and Born predictions for the cross sections at 1 eV, and the fraction of the cross section, f_{BD}^{-1}, accounted for by the Born model.

[a] Infrared inactive mode; provides no contribution to D_n.

corrected value of D_n from Table 1, that is smaller than $D_n = 0.126$ a.u. used in [20]), and about 10–15% larger at 1.05 eV. This discrepancy is qualitatively similar to that observed in Fig. 2 (left panel), where the BDM prediction is smaller than the measured integral positron-impact cross section.

Electron-impact DCS data are available for CO at 1 eV [16], and also for CH_4 at 1 eV ($\nu_2 + \nu_4$ modes, not resolved) and at 2 eV ($\nu_2 + \nu_4$ and $\nu_1 + \nu_3$ modes) [19]. These DCS show evidence of forward peaking consistent with Eq. (1). In fact, the data for CO of [17] show that experiment and the BDM agree well at 20° below 1 eV. However, the measured cross sections for both CO and CF_4 are consistently higher than the BDM values at larger angles ($\theta > 30°$). This is particularly true for the $\nu_2 + \nu_4$ modes of CH_4. At higher energies in CO, the DCS are quite different than the prediction of the Born model due to a prominent $^2\Pi$ electron shape resonance at 2 eV. These observations and a comparison with calculated integral cross sections presented in [16,17,19] suggest that the BDM underestimates the low-energy electron vibrational excitation cross section by a few tens of percent in CO and by up to a factor of two or more in CH_4.

The positron data shown in Figs. 3 and 4 point to even larger discrepancies. A possible explanation for this difference is that the positron-target interaction may be stronger than its electron counterpart (e.g. due to the strong virtual positronium correlations). Such an interaction affects the low partial waves, whose contributions dominate at low energies, while at higher energies the Born-dipole condition $kR \ll 1$ (R being the radius of the target) is violated, rendering the BDM inapplicable.

3. Summary and concluding remarks

Studies of state-resolved positron-impact cross sections for electronic and vibrational excitation of atoms and molecules is in its infancy, and the underlying physical excitation mechanisms have yet to be fully elucidated. In this paper, we have compared the limited set of vibrational cross sections measured to date with arguably the simplest excitation mechanism and theory, namely the Born-dipole model that considers only the long-range coupling of the induced molecular dipole with the Coulomb field of the positron, which is described by plane waves.

This Born-dipole approximation, with the dipole strength determined from infrared absorption data, was used to predict the absolute value of the cross sections for positron- and electron-impact. The results indicate that this dipole coupling is always significant (e.g. at the $\geqslant 18\%$ level), and in selected cases, the BDM model can explain most of the magnitude of the observed positron-impact cross sections. For all molecules studied except H_2, the BDM model predicts the shapes of the cross sections as a function of energy quite well. As stated above, whether this agreement is significant, even when the magnitudes of the BDM predictions are significantly smaller than the measurements, or is merely a coincidence, is presently unclear. We note that there is less data available for integral, state-resolved, electron-impact vibrational excitation cross sections than for the analogous positron cross sections, and relatively little of the latter. Further experimental work to make systematic comparisons of positron- and electron-impact cross sections would be of considerable interest.

Acknowledgement

This work is supported by the National Science Foundation, Grant PHY 02-44653.

References

[1] S.J. Gilbert, R.G. Greaves, C.M. Surko, Phys. Rev. Lett. 82 (1999) 5032.
[2] J.P. Sullivan, S.J. Gilbert, C.M. Surko, Phys. Rev. Lett. 86 (2001) 1494.
[3] J.P. Marler, C.M. Surko, Phys. Rev. A 72 (2005) 062702.
[4] N.F. Lane, Rev. Mod. Phys. 52 (1980) 29.
[5] A. Mann, F. Linder, J. Phys. B 25 (1992) 545.
[6] J.P. Sullivan, S.J. Gilbert, J.P. Marler, L.D. Barnes, S.J. Buckman, C. Surko, Nucl. Instr. and Meth. B 192 (2002) 3.
[7] S.J. Gilbert, C. Kurz, R.G. Greaves, C.M. Surko, Appl. Phys. Lett. 70 (1997) 1944.
[8] J.P. Sullivan, S.J. Gilbert, J.P. Marler, R.G. Greaves, S.J. Buckman, C.M. Surko, Phys. Rev. A 66 (2002) 042708.
[9] L.M. Bishop, L.M. Cheung, J. Phys. Chem. Ref. Data 11 (1982) 119.
[10] M. Hayashi, in: L.C. Pitchford et al. (Eds.), Swarm Studies and Inelastic Electron–Molecule Collisions, Springer, Berlin, 1987, p. 167.
[11] L.E. Kline, T.V. Congedo, Bull. Am. Phys. Soc. 34 (1989) 325.
[12] R.A. Bonham, Jpn. J. Appl. Phys. 33 (1994) 4157.
[13] M. Kimura, M. Takekawa, Y. Itikawa, H. Takaki, O. Sueoka, Phys. Rev. Lett. 80 (1998) 3936.
[14] F.A. Gianturco, T. Mukherjee, P. Paioletti, Phys. Rev. A 56 (1997) 3638.
[15] A. Jain, J. Phys. B 19 (1986) L379.
[16] J.C. Gibson, L.A. Morgan, R.J. Gulley, M.J. Brunger, C.T. Bundschu, S.J. Buckman, J. Phys. B 29 (1996) 3197.
[17] W. Sohn, K.H. Kochem, K. Jung, H. Ehrhardt, E.S. Chang, J. Phys. B 18 (1985) 2049.
[18] T. Nishimura, F.A. Gianturco, Phys. Rev. A 65 (2002) 062703.
[19] C.T. Bundschu, J.C. Gibson, R.J. Gulley, M.J. Brunger, S.J. Buckman, N. Sanna, F.A. Gianturco, J. Phys. B 30 (1997) 2239.
[20] K.-H. Kochem, W. Sohn, N. Hebel, K. Jung, H. Ehrhardt, J. Phys. B 18 (1985) 4455.