International Journal of Mass Spectrometry 192 (1999) 141–147

Excited state formation in studies of electron capture by state prepared doubly charged atomic ions

R.W. McCullough

Department of Pure and Applied Physics, The Queen's University of Belfast, Belfast BT7 1NN, Northern Ireland, UK

Received 4 January 1999; accepted 18 March 1999

Abstract

Electron capture by slow ($v < 1$ a.u.) partially stripped ions in atomic and molecular targets results in the selective formation of only a few excited states of either target or projectile and is highly sensitive to the internal energy carried by the projectile. This article describes a new experimental system employing the technique of double translational energy spectroscopy to study these state selective electron capture processes. Recent results involving slow C^{2+}, N^{2+}, and O^{2+} primary ions in prepared ground or metastable states, in collisions with simple atomic and molecular targets, are discussed. The results highlight the difficulties involved in the interpretation of previous studies where the projectile primary ion beams contained unknown mixtures of ions in both ground and metastable states. (Int J Mass Spectrom 192 (1999) 141–147) © 1999 Elsevier Science B.V.

Keywords: Low energy electron capture; State selective; State prepared ions; Translational energy spectroscopy; Metastable ions; Multiply charged ions

1. Introduction

Electron capture processes of the type,

$$X^{q+} + Y \rightarrow X^{(q-1)+}(n, l) + Y^{+}(n', l')$$

involving a wide variety of partially ionized species play an important role in both fusion [1] and astrophysical [2] plasmas. At impact velocities $v < 1$ a.u. where a quasimolecular description of the collision system is appropriate a limited number of product states can be formed effectively through pseudocrossings of the potential energy curves describing the initial and final molecular states [3]. Pseudocrossings in a limited range of internuclear separations provide the dominant contribution to the electron capture process, resulting in the formation of a relatively small number of excited product states.

A number of experimental techniques, such as photon emission spectroscopy (PES) [4] and translational energy spectroscopy (TES) [5], have been employed to study these low energy state selective electron capture (SSEC) processes involving partially stripped primary ions at kiloelectron volt energies. In the TES technique the difference ΔT between the kinetic energy T_1 of the primary X^{q+} ions and the kinetic energy T_2 of the fast forward-scattered $X^{(q-1)+}$ products is measured. This difference can be expressed as $\Delta T = (T_2 - T_1) = (\Delta E - \Delta K)$, where ΔK is the target recoil energy. Provided that

---

E-mail: rw.mccullough@qub.ac.uk

PII S1387-3806(99)00054-8

$\Delta E/T_1 \ll 1$ and the scattering is confined to small angles then $\Delta T \approx \Delta E$. Thus, within the limitations of the available energy resolution, an analysis of the $X^{(q-1)+}$ excited product yields in the energy change spectrum [6] enables relative cross sections for the main excited product channels to be determined. Those product channels associated with metastable ions, which might be present in the primary ion beams, can be identified using the TES technique. The observed energy change spectra may be dominated by such channels though a quantitative analysis is precluded unless the metastable content of the primary beam is known. The TES technique is of limited value in cases where the experimental energy resolution is insufficient to resolve ground and metastable product channels or where an accidental overlap in the energy defects exists. In addition if the metastable core is not conserved during the electron capture process then additional reaction channels may be opened [7]. The metastable content of the beam is dependent on the type of ion source used and the operating parameters. The importance of collision channels associated with metastable primary ions revealed by these TES studies also illustrates why many previous measurements of total electron capture cross sections carried out with ion beams of unknown metastable content in different laboratories exhibit large discrepancies [8,9].

The presence of metastables in the primary beam can often be seen in the energy change spectra in our previous studies of SSEC by TES [6] although, since the fraction present is usually not known, their influence is difficult to quantify. A number of methods, such as ion beam attenuation [10], optical attenuation [11] and translational attenuation [12], have been employed to determine the metastable fractions of primary ion beams to enable a quantitative analysis. However, in order to carry out measurements with ion beams in selected metastable or ground states, an approach based on double translational energy spectroscopy (DTES) can be employed. In this method, TES is first used in a suitable gas target to prepare and select product ions in the required ground or metastable state. These selected ions are then used in a second stage TES experiment. The DTES technique was first demonstrated [13] in the production of state selected beams of Ar^{2+} from Ar^{3+} + Ar collisions. However even though the existence of many metastable levels in Ar^{2+} made it difficult to produce pure state selected beams, the ability of the technique to provide much more information than from a single stage TES experiment was demonstrated.

Recently, in our laboratory we have successfully used the DTES technique to carry out SSEC studies with beams of pure ground state and pure metastable C^{2+} ions [14,15] and also with pure ground state N^{2+} ions [16,17]. More recently we have carried out studies with pure ground state and pure metastable O^{2+} ions [18]. Targets of He, Ne, Ar, H_2, N_2, and O_2 have been used with ion impact energies in the range from 1.75 to 8 keV. These results can be compared with previous measurements carried out with ion beams containing mixtures of ground and metastable ions.

Ratios of total one-electron capture cross sections for ground state and metastable C^{2+} ions in He, Ne, and Ar have also been determined using a simple beam attenuation technique.

2. Experimental approach

A schematic diagram of the double translational energy spectrometer is shown in Fig. 1. In order to illustrate the DTES technique the production of ^1S ground state or ^3P metastable C^{2+} ions is described.

A beam of C^{3+} ions was derived from a 5 GHz electron cyclotron resonance (ECR) ion source. The ions were formed within the source in a region held close to 0 V and then were extracted by a voltage of −4 kV applied to an extraction electrode and the beam transport tubes. The beam was focused, momentum analysed by a 90° double focusing electromagnet and then entered the first cylindrical electrostatic lens system L1 of the double translational energy spectrometer. The intensity of the C^{3+} ion beam at this stage was typically in the range 30–50 nA. After focussing and deceleration by L1 the beam passed through the hemispherical electrostatic energy analyser EA1 at an energy $40q$ eV (where $q = 3$). The emerging energy resolved beam (intensity ~0.2 nA and energy spread ~1 eV FWHM) was accelerated by

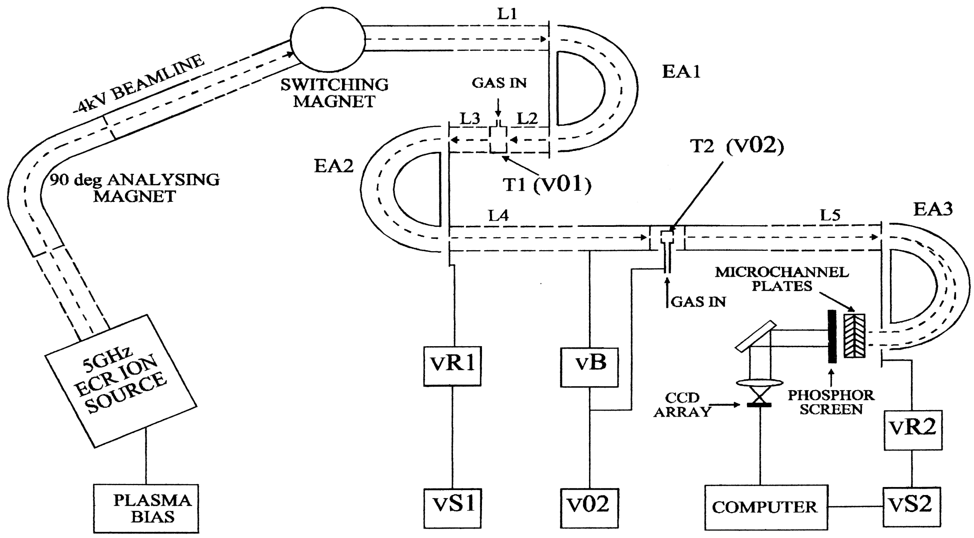

Fig. 1. Schematic diagram of the double translational energy spectrometer.

lens system L2 to an energy of qV_{01} eV. It then entered the first target gas cell T1 where the helium gas pressure was set to maximise the C^{2+} yield formed by one-electron capture collisions.

The C^{2+} forward scattered collisions products (in both ground and excited states) emerging from T1 were decelerated and focused by the lens system L3 before entering the hemispherical energy analyser EA2. Application of an appropriate positive bias voltage V_{R1} to EA2 and the associated lenses L3 and L4 ensured passage of C^{2+} ions while rejecting C^{3+} primary ions. The pass energy of EA2 was typically $60(q - 1)$ eV. In this work, for an initial $q = 3$, $V_{R1} = -V_{01}/(q - 1)$ with $V_{01} = -1000$ V. The translational energy change spectrum obtained by means of EA2 in this first stage of TES was used (by scanning the voltage V_{S1}) to identify and select C^{2+} ions in well defined energy states subject to the energy resolution limitations of the analyser. The principle is illustrated by the TES energy change spectrum shown in Fig. 2 for one-electron capture in C^{3+}–He collisions at 3 keV obtained using C^{3+} ions directly from the ECR ion source. The spectrum is in good accord with that observed in our previous work [19]. The collision product channels associated with the peaks A, B, C, and D in this spectrum are detailed in Table 1.

In order to use DTES to select a beam of ground state C^{2+} $(1s^2 2s^2)^1S$ ions the first stage of TES can be used to select ions from peak A. This corresponds to capture into C^{2+} $(1s^2 2s 2p)^1P$ which has a lifetime of only 0.53 ns [20] and decays by an optically

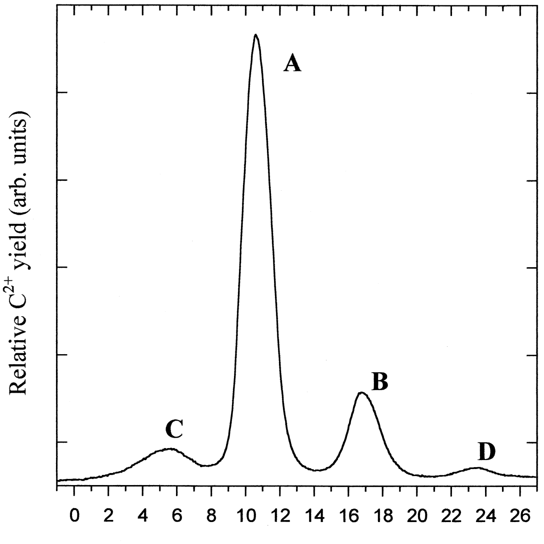

Fig. 2. TES energy change spectrum of C^{2+} ions formed in one-electron capture by 3 keV C^{3+} ions in collisions with He using C^{3+} ions obtained directly from the ECR ion source.

Table 1
Collision product channels corresponding to peaks A, B, C, and D in the TES energy change spectrum (Fig. 2) for one-electron capture by 3 keV C^{3+} ions in collisions with He

Channel	Product channel	Defect (eV)
D	C^{2+} $2s^2(^1S)$ + He^+ (^2S)	23.28
B	C^{2+} $2s2p(^3P)$ + He^+ (^2S)	16.78
A	C^{2+} $2s2p(^1P)$ + He^+ (^2S)	10.59
C	C^{2+} $2p^2(^3P)$ + He^+ (^2S)	6.24
	C^{2+} $2p^2(^1D)$ + He^+ (^2S)	5.20

allowed transition to the ground state before reaching the second target. In the same way, in order to select a beam of metastable C^{2+} $(1s^22s2p)^3P$ ions, the scanning voltage V_{S1} can be changed by approximately 3 V (corresponding to 6 eV) to allow ions comprising peak B to pass. As this state has a long lifetime of 12.5 ms [21], less than 0.1% of these ions will decay in the flight time (~10 μs) between the first and second targets. The peaks in this particular energy change spectrum (Fig. 2) can be seen to be well separated and can be cleanly resolved within the ~1 eV resolution of EA2. A 100% pure beam of C^{2+} ^1S ground or ^3P metastable ions could therefore be produced by application of an appropriate scanning voltage V_{S1}.

The state selected C^{2+} beam emerging from EA2 was then accelerated and focused by lens system L4 into the main target gas cell T2. This was 9 mm long with entrance aperture 1.2 mm diameter and exit aperture 1.9 mm diameter. The collision energy E_C in the cell T2 is given by $E_C = -[V_{01} + (q - 1)V_{02}]$ eV where in the present work, for an initial $q = 3$, $V_{01} = -1000$ V and $V_{02} = -1500$ V. The gas flow rate to T2 was kept low enough to ensure the C^+ ions were formed as a result of one-electron capture in single collisions. The potential difference V_B applied between the target cell housing and the target cell T2 ensured that only C^+ ions formed within the target cell T2 contributed to our measured energy change spectra.

The forward scattered C^+ product ions emerging from T2 were decelerated and focused by lens system L5 into EA3, the final energy electrostatic energy analyser, which had a half angle acceptance of 0.5°. Checks were made as in our earlier work [6] to ensure that this acceptance angle was sufficient to avoid any significant loss of scattered particles. As in the case for capture in the target cell T1, appropriate potentials were applied to L5 and EA3 to allow product C^+ ions to enter with an energy of $40(q - 2)$ eV. The required retarding voltage is given by $V_{R2} = -(V_{01} + V_{02})/(q - 2)$. The forward scattered C^+ product ions emerging from the target cell T2 were energy analyzed by EA3 and counted by a computer controlled position sensitive detector system.

In the present work, energy change spectra (to be discussed in Sec. 3) were obtained for pure 4 keV beams of C^{2+} $(1s^22s^2)$ ^1S ground state and pure metastable C^{2+} $(1s^22s2p)$ ^3P ions in He, Ne, and Ar using DTES. These spectra could be compared with the corresponding TES spectra obtained using C^{2+} ions of unknown metastable content obtained directly from the ECR ion source. The energy scales on our energy change spectra were calibrated to an accuracy of better than 0.2 eV by reference to our previous TES measurements for one-electron capture in C^{2+}–Ar collisions [19] and to energy defects for the various product channels obtained from energy level tabulations [22,23]. Since the state C^{2+} $2s2p$ (^1P) decays rapidly (0.53 ns) to the ground state C^{2+} $2s^2$ (^1S) a pure ground state beam of C^{2+} can be produced by selecting channel 3. In contrast, due to the long (12.5 ms) lifetime of the C^{2+} $2s2p$ (^3P) state, selecting channel 2 enabled us to produce a beam of metastable ions. Therefore a 100% pure beam of C^{2+} ^1S ground or ^3P metastable ions can be produced by a simple adjustment of the analyser bias voltage. These state prepared beams then enter a second stage target cell, held at the required collision voltage, from which final product states are determined by the final electrostatic analyser and position sensitive detector system in the form of an energy change spectrum.

3. Results and discussion

To date, SSEC has been studied at collision energies in the range 1.75–8 keV involving state prepared ions of C^{2+}, N^{2+}, and O^{2+} in a variety of atomic and molecular targets. The progress that has been made in

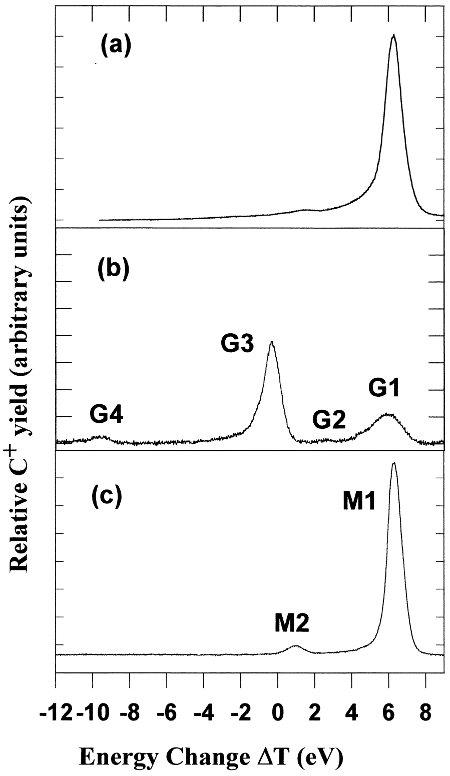

Fig. 3. Energy change spectra for one-electron capture from He by 4 keV C^{2+} ions (a) derived directly from our ECR ion source, (b) TES prepared ^1S ground state ions, and (c) TES prepared ^3P metastable ions.

improving our understanding of these slow one electron capture collisions, which are extremely sensitive to the amount of internal energy carried by the incident ion, is evident from the following representative selection of data.

3.1. Studies involving C^{2+} ions

Fig. 3 shows a TES energy change spectrum obtained from a He target using a 4 keV C^{2+} derived directly from our ECR ion source which is compared with the energy change spectra using DTES for pure C^{2+} ^1S ground state and pure C^{2+} ^3P metastable ion beams. The DTES measurements provide more detailed information than recent TES measurements on the C^{2+} + He system carried out with primary beams of unknown metastable content [24].

Our measured ratio of 11.5 ± 3.0 for the total one-electron capture cross sections $\sigma(^3P)/\sigma(^1S)$ at 4 keV derived from beam attenuation measurements may be compared with a previous estimate of 9.7 ± 2.4 based on beam attenuation in conjunction with controlled ion source electron impact energies [8]. Theoretical calculations [25] predict a ratio of about 15. We have used our measured ratio $\sigma(^3P)/\sigma(^1S)$ at 4 keV to estimate the metastable fraction f in the “mixed beam” derived directly from the ECR ion source. By changing the ion source conditions values of f ranging from 0.25 to 0.45 were obtained. Similarly large C^{2+} metastable fractions of 0.55 from a 10 GHz ECR ion source were measured [26] compared with a calculated [27] fraction of 0.56.

Since the total one-electron capture cross sections in He for 4 keV C^{2+} ^3P metastable ions are considerably larger than the corresponding cross sections for ^1S ground state ions cautious interpretation is required of any previous measurements with ion beams of unknown metastable content.

3.2. Studies involving ground state N^{2+} ions

SSEC studies have been carried out using pure beams of ground state N^{2+} ions in targets of He, Ne, and Ar [16] and in H_2 [17] in the energy range 1.75–8 keV.

Energy change spectra were obtained at collision energies in the range 1.75–8.0 keV. To ensure a pure N^{2+} (^2P) ground state primary ion beam: the energy resolution was about 1 eV. For comparison, TES measurements were also carried out using N^{2+} ions obtained directly from the ECR ion source. In this case the energy resolution was about 0.7 eV. The two sets of energy change spectra may be compared in Fig. 4.

The pure ground state and “mixed” N^{2+} beam energy change spectra in Fig. 4 exhibit significant differences. In particular, while our pure ground state spectra can be interpreted unambiguously, the prominent peak M2, at around 7 eV in the mixed beam spectra, accounts for around 25% of the total N^+ yield illustrating the strong influence of an unknown admixture of metastable ions. Many channels, including dissociative one-electron capture involving the H_2^+ A

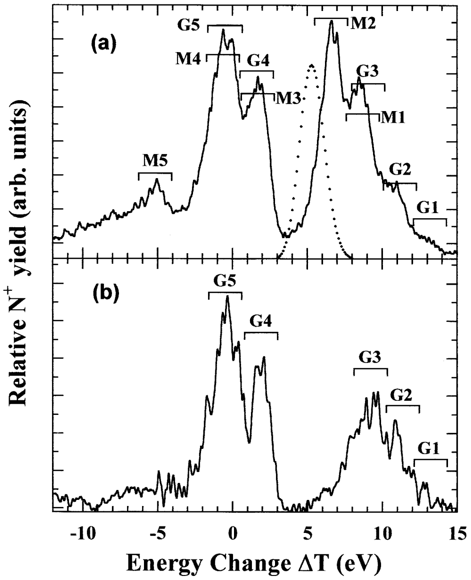

Fig. 4. Energy change spectra at 8 keV for one-electron capture in N^{2+}–H_2 collisions using (a) a N^{2+} beam obtained directly from the ion source (b) a pure beam of $N^{2+}(^2P)$ ground state primary ions using DTES. The peaks G and M correspond to product channels involving ground and metastable N^{2+} primary ions, respectively. The energy defects shown allow for vibrational excitation of H_2^+ ($\nu = 0 \rightarrow$ DL), where DL is the dissociation limit.

$^2\Sigma_u^+$ repulsive state, contribute to the long endothermic tail, which is less prominent in the pure ground state spectrum.

Results of previous TES studies [28] at few kiloelectron volt energies exhibit significant discrepancies both in the structure and peak designations of the observed energy change spectra, which were interpreted in terms of an assumed mainly ground state N^{2+} (^2P) primary ion beam.

3.3. Studies involving ground state O^{2+} ions

Recently, we have obtained data for SSEC by 4 keV ground state O^{2+} ions in targets of He, Ne, and Ar. Fig. 5 shows energy change spectra for pure ground state ^3P and metastable ^1D ion beams in collision with He at 4 keV. The associated product channels are listed in Table 2.

The main peaks G1, G2, and G3 associated with collisions involving ground state primary ions can be clearly identified and distinguished from peaks M1 and M2 which are associated with collisions involving metastable ions. Here we confirm at 250 eV u^{-1} the dominance the ^2D (G2) channel over the ^2P (G1) channel which was predicted in a recent theoretical treatment [29] using a quantum mechanical calculation of the collision dynamics. An earlier quantum mechanical description using a second order distorted-wave approximation [30] predicted that the capture process is dominated by the ^2P channel. This clearly demonstrates the effectiveness of DTES where previously poorly resolved TES measurements [31] have resulted in doubt over some peak assignments. Further work on this system is in progress.

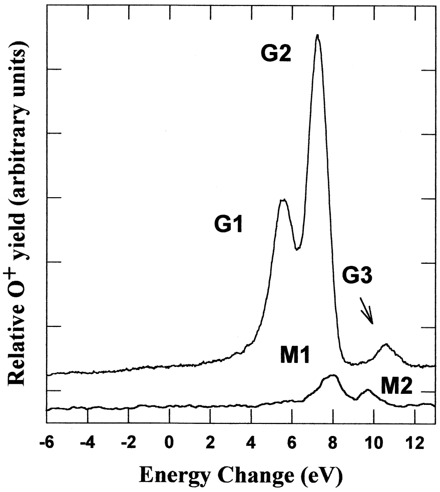

Fig. 5. Energy change spectra for 4 keV O^{2+} pure ground state ^3P (G) and metastable ^1D (M) ion beams in collisions with He.

Table 2
Main reaction channels for one-electron capture by ground state O^{2+} ^3P ions and metastable O^{2+} ^1D ions in collisions with helium at 4 keV

Peak	Product channel	Energy defect (eV)
G1	O^+ $(2p^3)^2P$ + He^+ (^2S)	5.51
G2	O^+ $(2p^3)^2D$ + He^+ (^2S)	7.21
G3	O^+ $(2p^3)^4S$ + He^+ (^2S)	10.53
M1	O^+ $(2p^3)^2P$ + He^+ (^2S)	8.02
M2	O^+ $(2p^3)^2D$ + He^+ (^2S)	9.72

4. Conclusions

These results, when compared with previous TES measurements, clearly illustrate the effectiveness of the DTES technique. The results highlight the role of metastable contributions in previously measured total one electron capture cross sections and demonstrate that, in some cases, a small fraction of metastable ions in the primary ion beam may be responsible for the majority of the product ions. The DTES technique will allow for the first time a detailed comparison with theoretical predictions without the ambiguity of these unknown fractions of metastable primary ions contributing to the energy change spectra. The results of these DTES studies demonstrate that previous experimental measurements of TES spectra and total one electron capture cross sections may contain significant contributions due to these metastable ions in the primary ion beams used in the experiments. Work is currently in progress in our laboratory to resolve this problem, particularly in the case of atomic hydrogen targets.

Acknowledgements

This article is dedicated to the memory of Professor John Geddes, a friend and colleague (died suddenly 4 December 1998) whose contribution to this work is gratefully acknowledged. The research was part of a Programme Grant programme supported by the UK Engineering and Physical Sciences Research Council. The author also gratefully acknowledges the contributions of D. Burns, Dr. J.B. Greenwood, Dr. W.R. Thompson, D. Voulot, and Professor H.B. Gilbody to this work. The award of Research Studentships from the Department of Education for Northern Ireland and the European Social Fund is also acknowledged.

References

[1] R.K. Janev, IAEA Report No. INDC(NDS)-277, 1993.
[2] T.E. Cravens, Geophys. Res. Lett. 24 (1997) 105.
[3] R.K. Janev, H.P. Winter, Phys. Rep. 117 (1985) 265.
[4] R. Hoekstra, J.P.M. Beijers, A.R. Schlatmann, R. Morgenstern, F.J. de Heer, Phys. Rev. A 41 (1990) 4800.
[5] H.B. Gilbody, Advances in Atomic, Molecular Physics and Optical Physics, B. Bederson, H. Walther (Eds.), Academic Press, New York, 1994, Vol. 32, p. 149.
[6] R.W. McCullough, F.G. Wilkie, H.B. Gilbody, J. Phys. B: At. Mol. Opt. Phys. 17 (1984) 1373.
[7] J.P.M. Beijers, R. Hoekstra, R. Morgenstern, F.J. de Heer, J. Phys. B: At. Mol. Opt. Phys. 25 (1992) 4851.
[8] E. Unterreiter, J. Schweinzer, H.P. Winter, J. Phys. B: At. Mol. Opt. Phys. 24 (1991) 1003.
[9] H.P. Winter, J. Phys. Chem. 99 (1995) 15448.
[10] H.B. Gilbody, Inst. Phys. Conf. Ser. 38 (1977) 156.
[11] A. Matsumoto, S. Ohtani, T.J. Iwai, Phys. B: At. Mol. Opt. Phys. 15 (1982) 1871.
[12] B.A. Huber, H.J. Kahlert, J. Phys. B: At. Mol. Opt. Phys. 16 (1983) 4655.
[13] B.A. Huber, H.J. Kahlert, K. Wiesemann, J. Phys. B: At. Mol. Opt. Phys. 17 (1984) 2883.
[14] J.B. Greenwood, D. Burns, R.W. McCullough, J. Geddes, H.B. Gilbody, J. Phys. B: At. Mol. Opt. Phys. 29 (1996) L599.
[15] J.B. Greenwood, D. Burns, R.W. McCullough, J. Geddes, H.B. Gilbody, J. Phys. B: At. Mol. Opt. Phys. 29 (1996) 5867.
[16] D. Burns, W.R. Thompson, J.B. Greenwood, R.W. McCullough, J. Geddes, H.B. Gilbody, J. Phys. B: At. Mol. Opt. Phys. 30 (1997) 4559.
[17] D. Burns, J.B. Greenwood, R.W. McCullough, J. Geddes, H.B. Gilbody, J. Phys. B: At. Mol. Opt. Phys. 30 (1997) L323.
[18] W.R. Thompson, Phys. Scr., to be published.
[19] M. Lennon, R.W. McCullough, H.B. Gilbody, J. Phys. B: At. Mol. Phys. 16 (1983) 2191.
[20] W.L. Wiese, M.W. Smith, B.M. Glennon, Atomic Transition Probabilities, National Standard Reference Data Series 4, Vol. I, National Bureau of Standards, Washington, DC, 1966.
[21] K.T. Cheng, Y.K. Kim, J.P. Desclaux, At. Data Nucl. Data Tables 24 (1979) 111.
[22] S. Bashkin, J.O. Stoner, Atomic Energy Levels and Grotrian Diagrams, North-Holland, Amsterdam, 1978.
[23] R.L. Kelly, ORNL Report No. 5922, Oak Ridge National Laboratory, USA, 1992.
[24] A.R. Lee, A.C.R. Wilkins, C.S. Enos, A.G. Brenton, Int. J. Mass Spectrom. Ion Processes 134 (1994) 213.
[25] J.F. Castillo, I.L. Cooper, L.F. Errea, L. Mendez, A. Riera, J. Phys. B: At. Mol. Opt. Phys. 27 (1994) 5011.
[26] A. Brazuk, D. Dijkkamp, A.G. Drentje, F.J. de Heer, H.J. Winter, Phys. B: At. Mol. Opt. Phys. 17 (1984) 268.
[27] R.F. Welton, T.F. Moran, E.W. Thomas, J. Phys. B: At. Mol. Opt. Phys. 24 (1991) 3815.
[28] F.A. Rajgara, C. Badrinathan, D. Mathur, Int. J. Mass Spectrom. Ion Processes 85 (1988) 229.
[29] M. Gargaud, M.C. Bacchus-Montabonel, R. McCarroll, J. Chem. Phys. 99 (1993) 4495.
[30] S. Bienstock, T.G. Heil, A. Dalgarno, Phys. Rev. A 29 (1984) 503.
[31] A.R. Lee, A.C.R. Wilkins, C. Leather, A.G. Brenton, Phys. Rev. A 50 (1994) 1149.