ELSEVIER

00 November 2001

Chemical Physics Letters xxx (2001) xxx–xxx

CHEMICAL PHYSICS LETTERS

www.elsevier.com/locate/cplett

Influence of resonant scattering on electron-swarm parameters in NO

L. Josić [a], T. Wróblewski [b], Z.Lj. Petrović [a], J. Mechlińska-Drewko [c], G.P. Karwasz [b,d,*]

[a] *Institute of Physics, P.O. Box 68, 11080 Zemun, Yugoslavia*
[b] *Institute of Physics, Pomeranian Pedagogical Academy, 76200 Słupsk, Poland*
[c] *Faculty of Applied Physics and Mathematics, Technical University, 80952 Gdańsk, Poland*
[d] *Istituto Nazionale per la Fisica della Materia, Unità di Trento, 38050 Povo-TN, Italy*

Received 13 August 2001

Abstract

A semiempirical analysis of low-energy electron scattering in nitric oxide has been performed. The deduced set of total and partial cross-sections has been used to calculate the ratio of electron transversal diffusion to mobility at low and intermediate reduced electric fields. The modelling gives indications for high values of vibrational cross-section in the 0.7–1.2 eV energy range that can be explained assuming presence of two resonant states, the first one similar to the low-energy $^2\Pi_g$ resonance in O_2, the second one resembling the $^2\Pi_g$ resonant state in N_2. © 2001 Published by Elsevier Science B.V.

1. Introduction

Nitrous oxide (NO) is of an essential importance for atmospheric processes [1], air pollution control [2] and biophysics [3]. A renewed interest has been recently observed for electron scattering on this molecule [4–7] (see [8] for a review of earlier data). In particular, precise measurements of total electron-scattering cross-sections down to 0.2 eV have been published [5], showing a resonant structure much more pronounced than that observed in earlier determinations [9,10]. Available sets of total and partial cross-sections used for plasma modelling [11,12] do not take into account these recent results. In particular, there are large uncertainties regarding the vibrational excitation in NO – absolute cross-section measurements cover solely the energy range from 7.5 to 40 eV [13].

Knowledge of the vibrational cross-sections is needed for modelling processes involving the recombination of the NO^+ ion in low-temperature plasmas and atmosphere [14,15]. It was noticed already in early works [16,17] that the very-low-energy vibrational cross-section shows some resonant structures but the techniques used (electron trap [16] and differential scattering measurements

* Corresponding author.
E-mail address: karwasz@science.unitn.it (G.P. Karwasz).

0009-2614/01/$ - see front matter © 2001 Published by Elsevier Science B.V.
PII: S0009-2614(01)01310-0

[17]) did not allow evaluation of the integral cross-sections. In particular, the electron-trap method managed to determine well relative proportions between different vibrational channels in the case of O_2 but not in NO, due to a specific overlap of energy levels in NO and NO^- [16]. As for N_2 [18,19] and O_2 [20] several measurements of vibrational cross-sections below 1 eV have been performed; we are not aware of recent very-low-energy electron-beam data in NO. From the theoretical side much progress has been recently made in understanding the dynamics of the low-energy resonant scattering on diatomic targets [21]. However, the theory is still rather unsuccessful in predicting total cross-sections for resonant scattering even in N_2 [18]. Swarm experiments constitute an alternative way of evaluating low-energy electron-scattering cross-sections.

Recently, we have measured [22] the ratios of the transverse diffusion coefficient to the mobility D_T/μ and of the longitudinal diffusion coefficient to mobility D_L/μ in NO for the reduced fields between 10 Td and 300 Td (1 Td = 10^{-21} V m^2), see Fig. 1. In a rough evaluation performed in that work with the use of Boltzmann analysis we have shown that the generally acknowledged set of elastic and inelastic cross-sections in NO [11] does not reproduce the experimental values of characteristic energies. In particular, big discrepancies occur below 10 Td, i.e. in the range corresponding to the mean electron energies of few eV range.

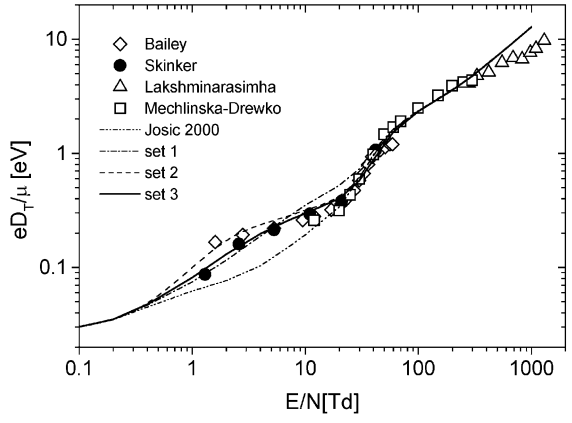

Fig. 1. Comparison between present models and experimental determinations of the D_T/μ coefficient in NO. Points: [22,31–33]. Lines: [23] and three present models, see also Fig. 3.

We have verified in a preliminary study [23] that a correction factor as high as 40 would be needed for the $v = 1$, 2, 3 cross-sections of Spence and Schulz [16] in order to reproduce the experimental drift coefficients. In different models [2,12] some arbitrary corrections to the early vibrational cross-section data [16] were applied in order to fit the transport data available at that moment. In the present work we perform a detailed analysis of elastic and inelastic electron scattering on NO, yielding a set of cross-sections in good agreement with the recent beam experiments [5,6] on one side, and reproducing well the transport coefficients in a wide range of reduced electrical fields, on the other side.

2. Resonant scattering in diatomic gases

Electron scattering in NO at low energies presents some unique features in comparison to other diatomic gases. Total cross-sections in the four diatomic molecules N_2, O_2, CO and NO assume similar values at energies above 10 eV [10]. Analogies exist also between elastic (see [8]) and ionization [24] cross-sections. However, at about a few eV, the total and partial cross-sections in these four targets differ substantially, due to a different nature of the resonant scattering.

For the N_2 molecule a $^2\Pi$ shape resonance shows up as a wide maximum in the total cross-section between 1.8 and 3.6 eV, with a vibrational structure superposed [18]. The vibrational excitation constitutes about one-third of the resonant part of the total cross-section, both for CO and N_2 (see [8]). The partitioning into separate vibrational channels in N_2 is rather equal: the successive maxima for the $v = 1$ to $v = 5$ excitations diminish by relative factors from 0.6 to 0.8 [8,19].

The low-energy, long-lived $^2\Pi$ resonance in O_2 shows up as a series of narrow maxima in the 0.3–1.2 eV range. These maxima, at energies corresponding to the vibrational levels of the transient O_2^- state, were observed in the total [25], elastic and vibrational [20] cross-sections. The maxima of the integral vibrational cross-sections in O_2 scale

down with rising v by large factors, varying from 3 to 10 (see [20]).

Resonant structures in NO between 0.4 and 1.6 eV were observed already in early experiments: in electron transmission spectra and in the zero-angle scattering functions for excitation of $v = 1$, 2, 3 vibrational levels [26], in 180° and 20° scattering-angle differential elastic cross-sections [27,28]. From that evidence and in particular from detailed measurements of elastic and vibrational ($v = 1$–5) differential cross-sections at 0.2–2.5 eV energy [17] the existence of three overlapping resonant states was deduced [29].

The lowest lying of the NO^- states, the $^3\Sigma^-$ one, is a shape resonance, i.e. caused by the temporary capture of an incoming electron into a free orbital of the molecule in its fundamental electronic state. The two higher states $^1\Delta$ and $^1\Sigma^+$ are 'core-excited' states, i.e. involve the molecular target in electronically excited states. As the transient NO^- state is isoelectronic with the O_2 molecule the configurations of these core-excited resonances should be analogues to the two lowest electronically excited states of O_2, i.e. the $a^1\Delta_g$ and $b^1\Sigma_g^+$ ones (0.977 and 1.626 eV excitation energies, respectively). Teillet-Billy and Fiquet-Fayard [29] analysing vibrational cross-section measurements in NO [17] placed the shape, $^3\Sigma^-$ state at zero energy and the $^1\Delta$ state at 0.75 eV. Tenysson and Noble [30] from six-state R-matrix calculations obtained the following energies of the three resonances in NO: −0.52, +1.4 and +2.3 eV for the $^3\Sigma^-$, $^1\Delta$ and $^1\Sigma^+$ states, respectively.

The two recent beam experiments on NO, the high-resolution total cross-sections measurements [5] and the ultra-low-energy large-angle elastic measurements [6] give some more stringent conditions for predicting elastic and vibrational cross-sections below 2 eV. In particular Randell et al. [6] pointed out that the series of narrow (25–30 meV FWHM) peaks in the differential elastic cross-section, with the first one at 0.13 eV and 0.16 eV spacing, overlaps with another series, of wider peaks (60–70 meV), with the first one at 0.77 eV. Alle et al. [5] gave absolute values of the total cross-section with a 10% uncertainty, but were not able to observe the 0.13 eV peak, indicated already by measurements of Zecca et al. [9].

3. Model of NO cross-sections

In the present modelling different sets of cross-sections have been constructed with two restrains: to reproduce the experimental D_T/μ values [22,31–33] and to agree with the experimental values of total cross-sections [5]. The D_T/μ values were calculated from cross-sections using the two-term solution of the Boltzmann equation [34]. Momentum transfer cross-section was adjusted to fit the drift velocity data.

Characteristic energies (eD/μ) are particularly sensitive to the presence of inelastic processes in the scattering. However, swarm analysis based on the two sets of transport data does not provide unique results for a large number of inelastic channels and it also has a low-energy resolution at these energies. Therefore, some assumptions on cross-section shapes and in particular on partitioning between different vibrational channels are needed. Following the earlier predictions [29] and recent measurements [5,6] we expect the presence of two resonant series in the elastic and vibrational cross-sections.

A set of partial cross-sections used for the present modelling are shown in Fig. 2. For elastic cross-sections at low energies we have assumed a smooth, non-resonant 'background', obtained from low-energy total cross-sections in N_2 by normalizing to the total experimental value in NO at 3 eV [5]. A resonant structure is superposed on this background. The present elastic cross-section agrees well with recent absolute measurements [13]. Above 7.5 eV we have adopted the experimental vibrational $v = 1$ and $v = 2$ cross-sections by Mojarrabi et al. [13]. For electronic excitation we used recent experimental integral data [7], grouped for simplicity for similar energy loss, while for the ionization cross-section, we used the well-established measurements of [23].

In Fig. 3 we present two other sets (No. 1 and No. 2), out of numerous trials. They differ from the one shown in Fig. 2 by the amplitude of the vibrational cross-section in the 0.3–2.5 eV energy region. In different trials we changed the 'envelopes' and onsets of the resonances, the width of the peaks and the partitioning into different vib-

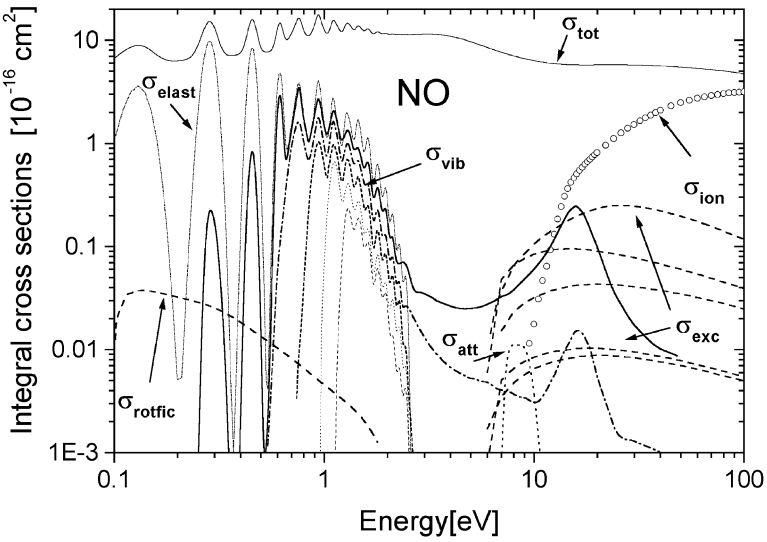

Fig. 2. A set of recommended integral cross-sections for electron scattering in NO. Total, elastic and vibrational, present model (set No. 3 in Fig. 3); rotational, present model – effective cross-section for the energy loss in rotational de-excitation and excitation; electron excitation, grouped for similar values of the energy loss, based on measurements by Brunger et al. [7]; ionization, [24]; electron attachment [4] and reference therein.

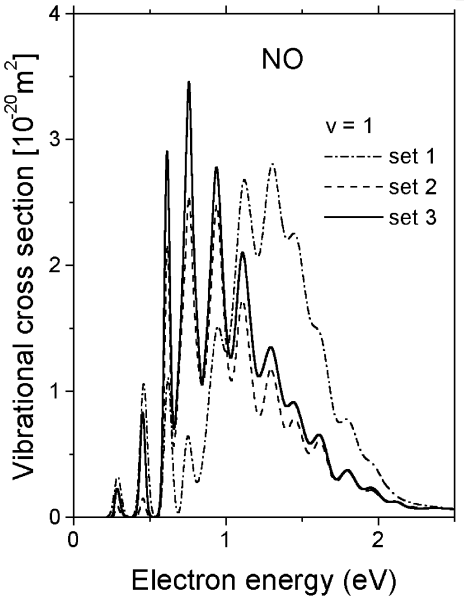

Fig. 3. Vibrational cross-section ($v = 0 \rightarrow 1$) for three alternative sets of integral cross-sections used for modelling the low-energy resonances, see text for details.

rational overtones. The D_T/μ curves corresponding to the three chosen sets are shown in Fig. 1.

In set No. 1 we assumed that the two resonances are well separated and the second one dominates, as it seemed from differential elastic measurements [6]. We adopted a constant partitioning ratio between subsequent vibrational channels (0.4 for the first resonance) and a high value of the summed vibrational cross-section. In set No. 2 we assumed that the amplitudes of the first two peaks in $v = 1$ are 1.5 times the values reported by Spence and Schulz [16], remaining therefore within the declared error bar. For the second resonance we assumed a similar shape to that used in set No. 3 but lower values (partitioning 0.5) of vibrational cross-sections.

Set No. 3 (recommended) is based on analogies between the NO, O_2 and N_2 resonances. First, we observe that in O_2 [20] the peaks in different v channels, including $v = 0$ show similar envelopes, with the first two peaks very low and the third or fourth being the highest, see Fig. 2 in [20]. We have adopted the O_2-like envelopes for the first resonance in NO with a 3:1:0.6 scaling between the maxima for subsequent channels $v = 0$, 1, 2, see

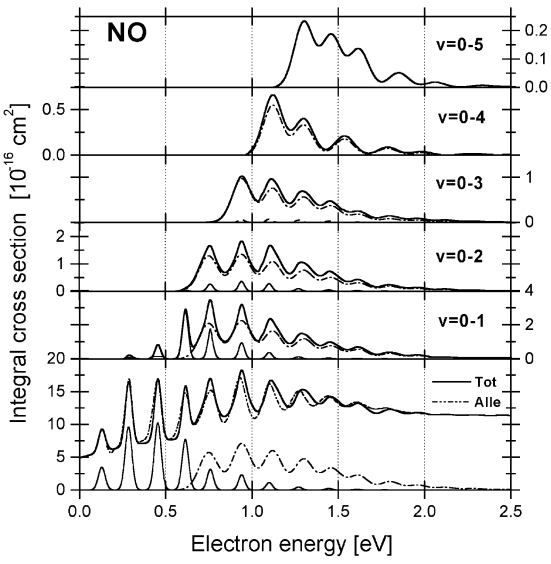

Fig. 4. Contributions from two resonances in NO into elastic and vibrational cross-sections in the resonance region (for set No. 3 in Fig. 3). Lowest panel: dash–dot–dot line, total experimental of Alle et al. [5] compared with total cross-sections from present model, thick line. All panels: thin lines, contributions from the first resonance; dash–dot lines, contributions from the second resonance.

our Fig. 4. Similarly to O_2, we assumed also that envelopes for different v channels reach maxima at different energies – onsets for the envelope curves have been chosen at respective thresholds for $v = 1$–5 curves and at the electron affinity (−0.29 eV) for the $v = 0$ channel.

Secondly, different trials have proved that in order to reproduce D_T/μ values in 5–50 Td high values of the vibrational cross-sections in the 0.6–1.2 eV energy range have to be assumed. In set No. 1, an O_2-like envelope was used also for the second resonance, with its amplitude at an 'upper limit' (the $v = 1$ cross-section at 1.12 eV coinciding with the $v = 0$ value). The model agrees well with the D_T/μ values at 1.1–10 Td but disagrees at 10–50 Td. More trials showed that these are 0.62, 0.76 and 0.94 eV peaks in $v = 1$ which determine a knee-like structure in D_T/μ at 10–50 Td. To accomplish a high value of $v = 1$ at 0.76 eV it was necessary to assume a different, N_2-like, envelope for the second resonance, rising quickly with energy above the threshold of the resonance and with high contribution from overtones. The assumed partitioning is somewhat similar to that in N_2: 0.8 for the $v = 1/v = 0$ ratio and 0.6 ratios for successive vibrational channels.

Set No. 3 assures a good agreement (within the experimental error bar) with the data of [22,31,33] in the whole 1–300 Td range, see Fig. 1. The low E/N data of [31] lie somewhat higher than the present model. We note also a good agreement with the only available (to our knowledge) beam-scattering data: Teillet-Billy and Fiquet-Fayard [29] reported an experimental value of 4.4×10^{-16} m^2 for $v = 1$ at the 0.9 eV peak, compared to 2.8×10^{-16} m^2 (and 3.2×10^{-16} m^2 at 0.75 eV) in our set No. 3.

4. Discussion

In spite of the overlap of resonances below 1.5 eV, the comparison with experimental swarm data assures a rather stringent test for the choice of the cross-sections. In particular, the D_T/μ values below 10 Td are very sensitive to the values of the vibrational cross-sections below 0.6 eV, i.e. in the energy region where only the first resonant state is present. We checked [23], for example, that a straightforward normalization of Spence and Schulz's cross-sections [16] by a constant factor can fit well the values at 20–300 Td but it underestimates the experimental [31,33] D_T/μ value at 3 Td by a factor of almost two (see dotted line in Fig. 1).

On the other hand, the 0.62 eV peaks in total [5] and elastic [6] cross-sections are lower than the 0.45 eV counterparts. In order to reproduce the 'knee' in D_T/μ values it is necessary to maximize the $v = 1$ cross-section at 0.6–0.9 eV. This can be done without introducing fictitious values of cross-sections assuming that in this region both the first and the second resonance contribute significantly to $v = 1$. This, in turn, requires the $v = 1$ envelope of the first resonance to be shifted in respect to the $v = 0$ envelope (in analogy to the O_2 resonance) and a quick rise of the second resonance envelope (in analogy to the $N_2{}^{-2}\Pi_g$ state).

As minor discrepancies, we note some shift between experimental [5] and present positions of resonant peaks at 0.9–2.0 eV. This can be caused by anharmonicity of the vibrational levels of the NO^- temporary state and/or by 'a boomerang effect' (see [18,21]) – due to a short lifetime of the resonance, like in N_2. Such shifting of peaks, however, does not influence the D_T/μ modelling. The present model disregards also a possible third resonance which seems to be visible in higher vibrational channels [17] and possible coupling effects between resonances.

At high E/N we observe a rising divergence between present model and experimental data of Lakshminarasimha and Lucas [32]. This is probably due to some underestimation of inelastic (electronic excitation and ionization) channels in our model. However, correction of the cross-section set at those energies is beyond the scope of this Letter and the choice of the cross-sections for electronic excitation [1,7] and ionization [24] does not affect the results for vibrational excitation obtained here.

The present analysis of electron diffusion coefficient in NO at low and intermediate reduced fields gives a strong indication for the overlap of two, quite different, resonant states below 2 eV. The first one, showing up as a series of narrow peaks in the total cross-section with the first one at 0.13 eV (see Fig. 2) and with a low rate of vibrational excitation, resembles the near-zero energy resonance in O_2. The second one, with an onset at 0.5–0.6 eV, shows wider peaks, with the first one being at 0.75 eV (see Fig. 4). In order to reproduce correctly the D_T/μ values at 10–50 Td, it is necessary to assume a very high contribution (1/3–1/2) of the vibrational excitation in the resonant total cross-section in the 0.6–1.0 eV energy range. Such a partitioning exceeds that for the $^2\Pi$ resonant state in N_2, but is similar to the one in $^2\Pi$ resonance in CO_2, see [35]. Alternatively, in order to reproduce the observed structures in the D_T/μ curve at low E/N, one should assume some 'threshold' peaks for the vibrational excitation in the 0.5–1.0 eV range. Such peaks were observed for polar molecules like HF, HCl, and HBr [21]. Experimental and theoretical validation of the presently deduced, somewhat 'phenomenological' vibrational cross-sections in the region of 1 eV is desirable.

Acknowledgements

One of the authors (ZLP) is grateful to Dr A.V. Phelps for suggesting this study many years ago and ZLP and LJ are grateful to the MNTRS project for partial funding.

References

[1] J.M. Ajello, K.D. Pang, B.O. Franklin, S.K. Howell, N.J. Bowring, J. Geophys. Res. 94 (1989) 9093.
[2] O. Eichwald, M. Yousfi, A. Hennad, M.D. Benabdessadok, J. Appl. Phys. 82 (1997) 4781 (and personal communication).
[3] S.H. Snyder, D.S. Bredt, Sci. Am. ((May)) (1992) 68.
[4] Y. Chu, G. Senn, P. Scheier, A. Stamatovic, F. Brünung, S. Matejcik, E. Illenberger, Phys. Rev. A 57 (1998) R697.
[5] D.T. Alle, M.J. Brennan, S.J. Buckman, J. Phys. B 29 (1996) L277.
[6] J. Randell, S.L. Lunt, G. Mrotzek, D. Field, J.P. Ziesel, Chem. Phys. Lett. 252 (1996) 253.
[7] M.J. Brunger, L. Campbell, D.C. Cartwright, A.G. Midelton, B. Mojarrabi, P.J.O. Teubner, J. Phys. B 33 (2000) 809.
[8] A. Zecca, G.P. Karwasz, R.S. Brusa, Riv. Nuovo Cimento 19 (3) (1996) 1.
[9] A. Zecca, I. Lazzizzera, M. Krauss, C.E. Kuyatt, J. Chem. Phys. 61 (1974) 4560.
[10] Cz. Szmytkowski, K. Maciag, G. Karwasz, Phys. Scr. 54 (1996) 271.
[11] A.V. Phelps, Compilation of Electron Cross Sections, JILA, University of Colorado, 1995. Available from <http://jilawww.colorado.edu/www/research/colldata.html>.
[12] M. Hayashi, in: Electron Collision Cross Sections, Handbook on Plasma Material Science, vol. 4, no. 9, 1992 (in Japanese)http://www.kinema.com/q_hayashi.dat.
[13] B. Mojarrabi, R.J. Gulley, A.G. Middleton, D.C. Cartwright, P.J.O. Teubner, S.J. Buckman, M.J. Brunger, J. Phys. B 28 (1995) 487.
[14] T. Mostefaoui, S. Laubé, G. Gautier, C. Rebrion-Rowe, B.R. Rowe, J.B.A. Mitchell, J. Phys. B 32 (1999) 5247.
[15] B.M. Penetrante, J.N. Bardsley, Phys. Rev. A 34 (1986) 3253.
[16] D. Spence, G.J. Schulz, Phys. Rev. A 33 (1971) 1968.
[17] M. Tronc, A. Huetz, M. Landau, F. Pochou, J. Reinhardt, J. Phys. B 8 (1975) 1160.

[18] W. Sun, M.A. Morrison, W.A. Isaacs, W.K. Trail, D.T. Alle, R.J. Gulley, M.J. Brennan, S.J. Buckman, Phys. Rev. A 52 (1995) 1229.
[19] M. Allan, J. Phys. B 18 (1985) 4511.
[20] M. Allan, J. Phys. B 28 (1995) 5163.
[21] P.L. Gertitschke, W. Domcke, Z. Phys. D 31 (1994) 171; M. Allan, M. Čížek, J. Horáček, W. Domcke, J. Phys. B 33 (2000) L209.
[22] J. Mechlińska-Drewko, W. Roznerski, Z.Lj. Petrović, G.P. Karwasz, J. Phys. D 32 (1999) 2746.
[23] L. Josić, Z.Lj. Pertović, J. Mechlińska-Drewko, D. Pliszka, G.P. Karwasz, in: Z.Lj. Petrović, M.M. Kuraica, N. Bibić, G. Malović (Eds.), Proceedings of the XX Symposium on Ionized Gases, Zlatibor, September 4–8, 2000, p. 111.
[24] D. Rapp, P. Englander-Golden, J. Chem. Phys. 43 (1965) 1464.
[25] S.J. Buckman, D.T. Alle, M.J. Brennan, P.D. Burrow, J.C. Gibson, R.J. Gulley, M. Jacka, D.S. Newman, A.R.P. Rau, J.P. Sullivan, K.W. Trantham, Austr. J. Phys. 52 (1999) 473.
[26] M.J.W. Boness, J.N. Hasted, Phys. Lett. 21 (1966) 526; I.W. Larkin, J.B. Hasted, J. Phys. B 5 (1972) 95.
[27] P.D. Burrow, Chem. Phys. Lett. 26 (1974) 265.
[28] H. Ehrhardt, K. Willmann, Z. Phys. 204 (1967) 462.
[29] D. Teillet-Billy, F. Fiquet-Fayard, J. Phys. B 10 (1977) L11.
[30] J. Tenysson, C.J. Noble, J. Phys. B 19 (1986) 4025.
[31] V.A. Bailey, J.M. Sommerville, Philos. Mag. 17 (1934) 1169.
[32] C.S. Lakshminarasimha, J. Lucas, J. Phys. D 10 (1977) 31.
[33] M.F. Skinker, J.V. White, Philos. Mag. 17 (1934) 1169.
[34] A.V. Phelps, L.C. Pitchford, Phys. Rev. A 31 (1985) 2932.
[35] J.C. Gibson, M.A. Green, K.W. Trantham, S.J. Buckman, P.J.O. Teubner, M.J. Brunger, J. Phys. B 32 (1999) 231.