International Journal of Mass Spectrometry 205 (2001) 111–117

Absolute cross sections for dissociative electron attachment to NF_3

D. Nandi, S.A. Rangwala, S.V.K. Kumar, E. Krishnakumar*

Tata Institute of Fundamental Research, Homi Bhabha Road, Mumbai 400 005, India

Received 20 March 2000; accepted 6 June 2000

Abstract

Absolute dissociative electron attachment cross sections for the formation of F^-, F_2^-, and NF_2^- from NF_3 have been measured in a crossed beams geometry by using the relative flow technique. Discrimination against ions with high kinetic energy are eliminated by employing a pulsed electron beam, pulsed ion extraction and a segmented time of flight mass spectrometer. The cross sections for the F^- formation, which is the dominant channel, is found to be almost a factor of 2 larger than what is reported earlier. This descrepancy is explained in terms of the discrimination against ions of appreciable kinetic energy in earlier measurements. (Int J Mass Spectrom 205 (2001) 111–117) © 2001 Elsevier Science B.V.

Keywords: Absolute cross sections; Dissociative electron attachment; NF_3

1. Introduction

The accuracies in the measurements of cross sections for any dissociative processes in molecules have been limited by the kinetic energies of the resulting fragments. This has been the situation particularly for electron impact processes like dissociative electron attachment (DEA) and dissociative ionization (DI), though there exist a few exceptions in which reliable absolute cross sections for DEA have been measured using the Tate and Lozier apparatus [1] for total ion cross sections [2]. In these exceptional cases, only one type of negative ion is produced and measurements could be carried out without mass analysis of the products. The use of a mass to charge ratio analysis becomes imperative for the measurement of partial cross sections when more than one type of ions are produced. However, in order to obtain absolute or even relative cross sections, it is necessary that the extraction, mass analysis, and the detection procedures for these ions are carried out without discriminating against their initial kinetic energies, angular distributions or their mass to charge ratios. These requirements are almost impossible to be met in the case of a gas cell which provide an extended source of ions, thus necessitating the use of crossed beams geometry employing a molecular beam and an electron beam, which provide an almost pointlike source of ions. Even with a point source of ions, it has been found that conventional mass spectrometers are not reliable in cross section measurements when the ions produced have appreciable initial kinetic energies [3]. An efficient solution to these problems was found in the use of a segmented time-of-flight

---

* Corresponding author. E-mail: ekkumar@tifr.res.in

Dedicated to Professor Aleksandar Stamatovic on the occasion of his 60th birthday.

PII S1387-3806(00)00270-0

(TOF) mass spectrometer along with the pulsed-electron-beam and pulsed-ion-extraction techniques and the relative flow technique. Such a combination has been used for both DEA and DI measurements for a number of molecules until now [4–10].

NF_3 is an important molecule from the point of view of various applications as a fluoride source in dry etching and in gas lasers. It has been shown that NF_3 plasma is very efficient in etching silicon and silicon dioxide. This has been explained as due to the relatively large dissociation of NF_3 as compared to CF_4 in a discharge [11]. A specific advantage of using NF_3 is the clean surface it provides as compared to the fluorocarbons which tend to give carbonaceous deposits on the etched surfaces. More recent work on NF_3 plasma has shown the importance of electron impact dissociation of NF_3 to the plasma chemistry as well as the etching of silicon [12].

So far there exist only two measurements on the absolute cross sections for DEA on this molecule [13,14]. And these differ by as much as a factor of 2. This discrepancy is a manifestation of the difficulties (as mentioned above) in making these measurements. Harland and Franklin [13] employed a linear TOF mass spectrometer where as Chantry [14] used a Tate and Lozier [1] apparatus, under the assumption that the ions resulting from the DEA process have relatively small kinetic energies. However, recent measurements on the ion kinetic energies [15] have shown that F^- ions are produced with appreciable kinetic energies (about 2 eV at electron energies close to the resonant peak). In view of this, the fact that the cross sections obtained by Chantry is about twice those obtained by Harland and Franklin is not surprising since a linear TOF mass spectrometer is more likely to discriminate ions of large kinetic energy as compared to a Tate and Lozier apparatus employed by Chantry. Considering the importance of NF_3 data and the fact that F^- ions are produced with relatively large kinetic energies, and that the measurements by Chantry were under the assumption of “modest” kinetic energies, we felt it necessary to make DEA measurements on this molecule with the more accurate technique presently available.

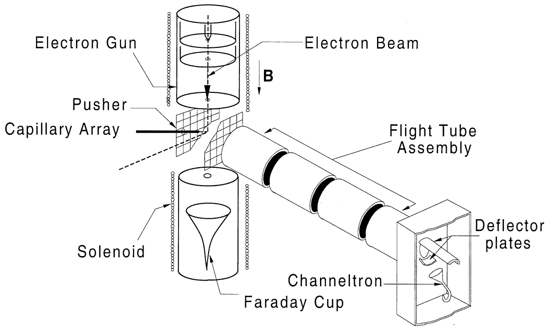

Fig. 1. Schematic of the experimental arrangement.

2. Experiment

The details of the experimental arrangement with slight variations and the method of measurement have been described in earlier publications [3,4,9,10]. However for the sake of completeness a summary is provided below.

The measurements were carried out in a crossed beams geometry employing a pulsed electron beam which intersected an effusive molecular beam at right angles (Fig. 1). The ions formed were extracted by a pulsed electric field into a segmented TOF spectrometer and detected by a channel electron multiplier operated in the pulse counting mode.

A heated tungsten filament was used to produce free electrons and they were formed into a beam using the Pierce geometry of cathode, grid and a grounded aperture. The electron beam was further collimated using the magnetic field (50 G) generated by a pair of solenoids immersed in the vacuum chamber. The gun, the interaction region, and the Faraday cup which is used for monitoring the electron current were mounted along the axis of these solenoids. The pulsing of the electron beam was carried out by initially cutting off the beam current by raising the negative bias on the grid with respect to the cathode and the filament and overriding it with a positive pulse of 1 ns rise time. The width of the pulse used in this experiment was about 300 ns. The molecular beam was produced by flowing the gas through a capillary array mounted at right angles to the electron beam.

The ions formed by the interaction were extracted by a pulsed electric field produced between two molybdenum wire meshes of 90% transmission placed symmetrically about the interaction region. The separation between them in the current experiment was 10 mm. The direction of the extraction field was at right angles to the electron beam direction and along the axis of the TOF mass spectrometer. The field was produced by applying a negative pulse of 200 V for a duration of 1 μs to the grid situated away from the TOF spectrometer. The timing of the pulse was such that it trailed the electron pulse by a few tens of nanoseconds so that the electron beam did not get affected by the large extraction field. This large extraction field ensured that all the ions produced with varying kinetic energies and angular distributions were brought into the TOF spectrometer within a narrow, though diverging cone. The segmented flight tube of the TOF spectrometer was designed to act as an electrostatic lens assembly such that the diverging beam of ions were transported to the detector without any loss. Since this experimental setup was used to carry out DEA to laser excited molecules, the channeltron was mounted off axis in order to shield it from the scattered UV laser photons. By applying a suitable voltage between two deflection electrodes mounted at the end of the flight tube assembly and before the detector, it was ensured that all the ions reached the detector.

The TOF mass spectra were obtained by using a time to amplitude converter (TAC) and a pulse height analyzer. Special care was taken to ensure that the overall count rate did not exceed one-tenth of the repetition rate of the electron gun pulsing so that pile up problems were negligible. This was particularly important since F^- ions were produced with very large intensities even at relatively low pressures. For measuring the excitation functions for individual ions, the appropriate time windows in the TAC were chosen and the data were stored in a PC using a General Purpose Interface Bus (GPIB) based data acquisition system which also controlled the electron energy. The measurement of the excitation functions for F_2^- and NF_2^- needed special attention since the cross section for the formation of F^- was a few orders of magnitude larger than those for these ions. Since F^- is the lightest of the three ions, the pulses due to it caused heavy pile up in the TAC at the pressures we needed to run the experiment for obtaining reasonable statistics for the other ions. This was overcome by applying appropriate delay for the "start pulse" of the TAC so that the pulses due to F^- did not get registered when the excitation functions for the ions of lower intensity was measured.

The excitation functions obtained for each type of ion was normalized to absolute cross section using the relative flow technique [16]. The basic principle behind this technique is to compare the relative intensities of the species of interest to that of a standard species of known cross section. In terms of the various experimental parameters, the equation governing this technique could be written as

$$\sigma(X^-/AX) = \sigma(Y^-/BY) \cdot \frac{N(X^-)}{N(Y^-)} \frac{F(BY)}{F(AX)} \frac{M_{BY}^{1/2}}{M_{AX}^{1/2}} \frac{I_e(BY)}{I_e(AX)} \frac{K(Y^-)}{K(X^-)} \tag{1}$$

where A, B, X, and Y represent atomic or molecular species and AX and BY, the parent molecules. N is the number of ions collected for a specific time, M is the molecular weight of the parent molecules, F is the flow rate, I_e is the electron current, σ is the cross section, and K is the detection efficiency which is a product of the efficiency with which ions are extracted from the interaction region, their transmission through the mass spectrometer and finally the efficiency with which they are detected. The overall efficiency as a function of the mass to charge ratio could be written as

$$K(m/e) = k_1k_2k_3 \tag{2}$$

where k_1 is the efficiency of extraction from the interaction region, k_2 is the efficiency of transmission through the mass analyzer, and k_3 is the efficiency of detection of the ion by the particle detector. In practice, it is difficult to isolate k_1, k_2, and k_3 and one measures only K. k_1 is independent of the mass to charge ratio, but depends on the initial kinetic energies and angular distributions of the fragment ions. k_1

could be made independent of these by applying large enough extraction field in the interaction regions so that all the ions are extracted into the mass spectrometer independent of the kinetic energies and angular distributions. The effect of such extraction fields on the electron beam could be eliminated only by pulsing the electron gun and the extraction field without any temporal overlap.

The transmission efficiency in the mass analyzer, k_2 is independent of *m/e* in a TOF spectrometer unlike in the case of a quadrupole mass spectrometer. However, k_2 could depend on the initial kinetic energies and angular distribution of the ions in the following way. Depending on the kinetic energies and angular distributions, the ions extracted from the interaction region will have finite divergence at the entrance of the mass spectrometer. In order to transport these ions to the detector without loss, one needs to use an electrostatic focusing lens assembly. This could be achieved by using the mass spectrometer itself as a focusing assembly. Thus in the present case, the flight tube of the TOF spectrometer is made of four separate elements and biased in such a way that the divergent beam of ions entering it is focussed at its exit where the detector is mounted. This lens system was designed using the SIMION program [17] by taking into account worst case kinetic energies and angular distributions and optimum extraction fields. Thus by appropriate choice of a multi-element TOF mass spectrometer we could make k_2 independent of *m/e* and initial kinetic energies and angular distributions.

The detection efficiency, k_3 of the ions by the channel electron multiplier has been found to depend on the velocity with which the ions strike the detector surface. Thus for a given acceleration, ions of smaller *m/e* will have larger detection probability [18]. In the case of measurements on positive ions, $k(m/e)$ can be determined using cross sections for the formation of singly charged ions from their respective noble gas atoms in the mass range from 4 to 132, by the relative flow technique [19]. But so far it has not been possible to apply it to the negative ions due to nonavailability of accurate cross sections in a wide *m/e* range. The only way to take care of the *m/e* dependence of K through k_3 is by increasing the nosecone voltages to such levels that there is saturation in the detection efficiency. It was found that a bias of 1500 V on the nosecone of the channeltron was sufficient to obtain saturation for the all the ions of relevence in the present measurements.

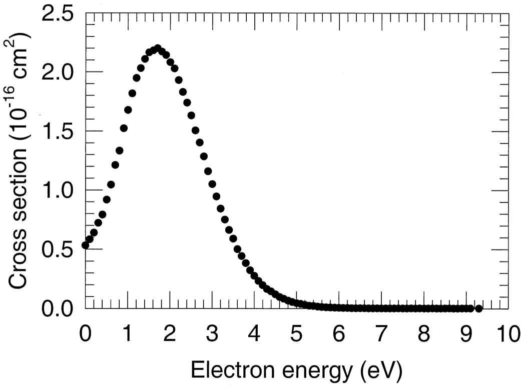

Fig. 2. Cross section for the formation of F^-.

The cross section for the formation of O^- from O_2 was used in the present case to calibrate the cross sections for the formation of F^-, F_2^- and NF_2^- formed from NF_3 as well as to calibrate the energy scale. An analysis of the various data on the formation of O^- from O_2 [20] have identified the results of Rapp and Briglia [2] as fairly accurate within an error of 10%. The uncertainty in the overall detection efficiency of the ions is estimated to be 5%. The uncertainty in the flow rate measurements is about 5% and the statistical errors in counting were 1% each in the case of F^- and O^- and about 5% in the case of F_2^- and NF_2^-. The error in the electron current measurement may have an upper limit of 5%. Considering all these, the combined error in the present measurements works out to be about 15%.

3. Results and discussion

It was found that F^- is the most dominant ion from the DEA process with very small intensities of F_2^- and NF_2^-. This is consistent with the earlier reports [13,14]. The cross sections for all the three species are given in Figs. 2, 3, and 4, and in tabular form in Table 1.

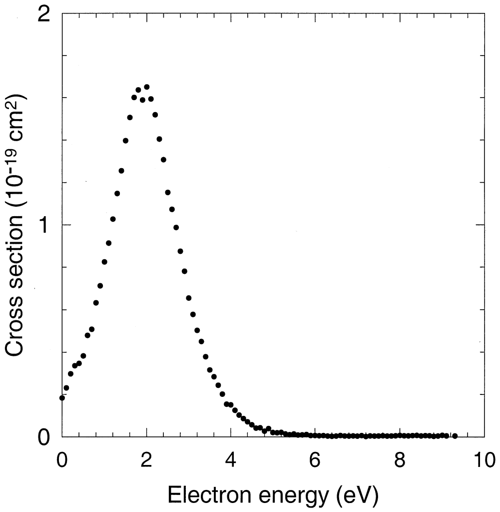

Fig. 3. Cross section for the formation of F_2^-.

The positions of the resonant peaks of all the three ions are in good agreement with the earlier reports. For all the ions, there is a finite cross section even at zero energy. This is unlike the results of Ruckhaberle et al. [15], but is similar to those by Harland and Franklin [13]. The high resolution measurements of Ruckhaberle et al. showed finite cross section for F^- at zero energy, where as both F_2^- and NF_2^- appear only above 1 eV. In the present measurements, as in

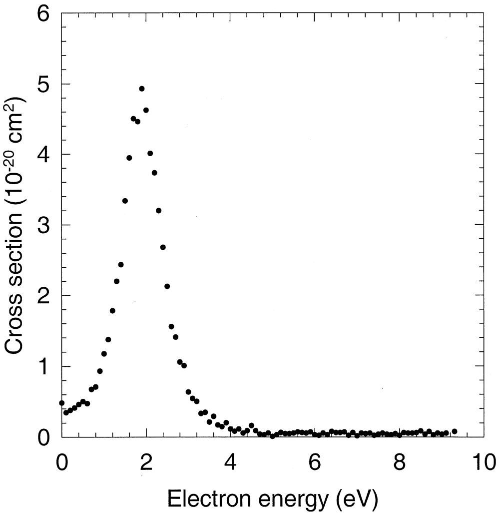

Fig. 4. Cross section for the formation of NF_2^-.

Table 1
Cross section for the formation of various ions from NF_3

Electron energy (eV)	σ (F^-) (10^{-16} cm^2)	σ (F_2^-) (10^{-19} cm^2)	σ (NF_2^-) (10^{-20} cm^2)
0.00	0.53	0.18	0.48
0.10	0.58	0.23	0.34
0.20	0.64	0.30	0.38
0.30	0.72	0.34	0.41
0.40	0.79	0.35	0.46
0.50	0.92	0.38	0.50
0.60	1.04	0.48	0.47
0.70	1.21	0.51	0.67
0.80	1.33	0.63	0.71
0.90	1.52	0.71	0.93
1.00	1.68	0.82	1.17
1.10	1.95	1.03	1.78
1.30	2.03	1.15	2.20
1.40	2.11	1.25	2.43
1.50	2.16	1.40	3.34
1.60	2.18	1.51	3.94
1.70	2.20	1.60	4.50
1.80	2.17	1.64	4.46
1.90	2.14	1.59	4.93
2.00	2.08	1.65	4.62
2.10	2.03	1.59	4.01
2.20	1.93	1.52	3.73
2.30	1.83	1.40	3.20
2.40	1.74	1.31	2.68
2.50	1.63	1.15	2.13
2.60	1.50	1.07	1.55
2.70	1.40	0.99	1.41
2.80	1.28	0.87	1.06
2.90	1.16	0.78	1.01
3.00	1.05	0.65	0.63
3.10	0.94	0.58	0.54
3.20	0.84	0.50	0.50
3.30	0.75	0.45	0.33
3.40	0.66	0.38	0.35
3.50	0.59	0.31	0.21
3.60	0.50	0.28	0.29
3.70	0.44	0.24	0.17
3.80	0.38	0.20	0.15
3.90	0.32	0.15	0.20
4.00	0.28	0.15	0.11
4.10	0.23	0.2	0.08
4.20	0.20	0.10	0.11
4.30	0.16	0.09	0.06
4.40	0.14	0.07	0.09
4.50	0.12	0.06	0.16
4.60	0.10	0.04	0.09
4.70	0.08	0.04	0.04
4.80	0.07	0.03	0.03
4.90	0.05	0.04	0.06
5.00	0.04	0.02	0.01
5.10	0.04	0.02	0.03
5.20	0.03	0.02	0.06

(continued on next page)

Table 1 (*continued*)

Electron energy (eV)	σ (F^-) (10^{-16} cm^2)	σ (F_2^-) (10^{-19} cm^2)	σ (NF_2^-) (10^{-20} cm^2)
5.30	0.02	0.01	0.05
5.40	0.02	0.01	0.05
5.50	0.02	0.01	0.06
5.60	0.01	0.01	0.07
5.70	0.01	0.01	0.06
5.80	0.01	0.01	0.06
5.90	0.01	0.01	0.07
6.00	0.01	0.01	0.03

the case of Harland and Franklin, the electron beam is not monochromatic and has a typical halfwidth of 0.5 eV. It is possible that the high energy tail of the electron energy distribution is giving rise to the finite cross section at zero energy for F_2^- and NF_2^-.

An interesting feature of the results is the relative sharpness of the NF_2^- peak as compared to F_2^- and F^-. For the sake of clarity, the excitation functions of all the three ions are given in Fig. 5, normalized to their peak intensities. The F^- and F_2^- peaks have a halfwidth of 2.4 and 1.9 eV respectively, whereas NF_2^- has a halfwidth less than 1 eV. One may argue that the smaller width is due to the late onset for their formation, as seen in the shift in the peak position with respect to F^-. This explanation may be valid for the case of F_2^- which has the same amount of shift in its peak position, but the falling edge of the peak is fairly close to that of F^- peak. However, in the case of NF_2^-, the peak seems to be squeezed from both the rising and falling edges with respect to that of F^-. Based on kinetic energy spectra of F^-, Ruckhaberle et al. has concluded that the observed resonance may be due to two anion states of the parent molecule, with vertical energies of 1.8 and 2.2 eV, respectively, from the neutral NF_3. They attribute the observed formation of F^- ions of lower kinetic energy at the incident electron energy of 2.2 eV to the dissociation of the higher state through a three particle break up (i.e. F^-, F, and NF). The relative absence of NF_2^- at higher energies, as seen from the narrowness of the peak could be due to propensity for the anion state at 2.2 eV to dissociate through this three body break up or a two body break up leading to F_2^- and NF, rather than F and NF_2^-. It will be interesting to pursue this problem further, based on Franck-Condon overlap and the dissociation limits for the two resonant states, if potential energy surfaces for the neutral as well as the resonances are available.

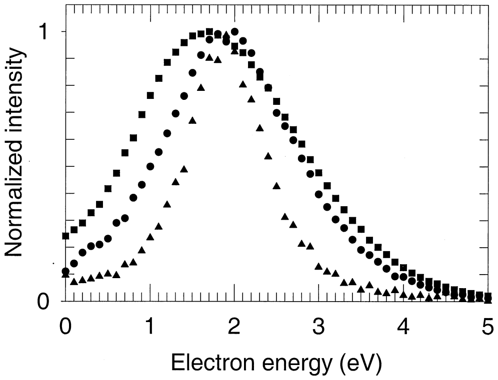

Fig. 5. Comparison of the excitation functions of F^-, F_2^-, and NF_2^-. The intensities are normalized at the respective peaks. Squares—F^-, circles—F_2^-, and triangles—NF_2^-.

As for the absolute cross sections, for F^- we obtain a value of 2.2×10^{-16} cm^2 as compared to 1.2×10^{-16} cm^2 reported by Chantry [14] and 0.6×10^{-16} cm^2 obtained by Harland and Franklin [13]. As pointed out by Harland and Franklin, their measurements were supposed to be an estimate of the cross sections in the absence of any other measurements. The measurements by Chantry was for the total cross section, and considering the cross section for the formation of F^- is a few orders of magnitude larger as compared to other ions, it may be treated as the F^- cross section. Chantry normalized the cross sections to absolute values using the cross section for O^- from N_2O as the standard "based on the expectation that F^- would be formed from NF_3 with only modest kinetic energy." The kinetic energy of O^- from N_2O is reported to have only 0.4 eV [21], whereas the kinetic energy measurements by Ruckhaberle et al. [15] gives an energy close to 2 eV for F^- formed at the resonant peak in NF_3. Considering the large difference in kinetic energies in the two cases, it is very likely that Chantry may have made a gross underestimation of the F^- cross section. Thus, a factor of 2 difference we observed in our data with respect to that measured by Chantry could be explained.

For F_2^-, the cross section we obtained is smaller than that obtained by Harland and Franklin, where as for NF_2^-, it is larger than the corresponding data, within a factor of 2. The source for disparity is not known except for the inherent difficulties in measuring relatively small cross sections, including the contributions due to the background gases. The cross sections reported by Chantry at a temperature of 365 K for both F_2^- and NF_2^- are much larger, i.e. in the range of 10^{-18} cm^2. It is not clear if the larger cross sections observed by him is due to temperature effect or due to varying ion detection efficiencies in his experiment.

Acknowledgement

The authors thank T.S. Ananthakrishnan from BARC for developing the data acquisition program.

References

[1] W.W. Lozier, Phys. Rev. 46 (1934) 268.
[2] D. Rapp, D.D. Briglia, J. Chem. Phys. 43 (1965) 1480.
[3] E. Krishnakumar, K. Nagesha, Rapid Commun. Mass Spectrom. 9 (1995) 336.
[4] E. Krishnakumar, K. Nagesha, J. Phys. B: At. Mol. Opt. Phys. 25 (1992) 1645.
[5] E. Krishnakumar, S.K. Srivastava, Int. J. Mass Spectrom. Ion Processes 113 (1992) 1.
[6] I. Iga, M.V.V.S. Rao, S.K. Srivastava, Z. Phys. D: Atoms, Mol., Clusters 24 (1992) 111.
[7] E. Krishnakumar, S.K. Srivastava, J. Phys. B: At. Mol. Opt. Phys. 27 (1994) L251.
[8] K. Nagesha, V.R. Marathe, E. Krishnakumar, Int. J. Mass Spectrom. Ion Processes 145 (1995) 89.
[9] E. Krishnakumar, S.V.K. Kumar, S.A. Rangwala, S.K. Mitra, Phys. Rev. A 56 (1997) 1945.
[10] S.A. Rangwala, S.V.K. Kumar, E. Krishnakumar, N.J. Mason, J. Phys. B 32 (1999) 3795.
[11] K.E. Greenberg, J.T. Verdeyen, J. Appl. Phys. 57 (1985) 1596.
[12] G. Bruno, P. Capezzuto, G. Cicala, P. Manodoro, J. Vac. Sci. Technol. A12 (1994) 690.
[13] P.W. Harland, J.L. Franklin, J. Chem. Phys. 61 (1974) 1621.
[14] P.J. Chantry, in Applied Atomic Collision Physics, H.S.W. Massey, E.W. McDaniel, B. Bedersen (Eds.), Academic, New York, 1982, Vol. 3, p. 35.
[15] N. Ruckhaberle, L. Lehmann, S. Matejcik, E. Illenberger, Y. Bouteiller, V. Perquet, L. Museur, C. Desfrancois, J.-P. Schermann, J. Phys. Chem. A 101 (1997) 9942.
[16] S.K. Srivastava, A. Chutjian, S. Trajmar, J. Chem. Phys. 63 (1975) 2659.
[17] D.A. Dahl, J.F. Delmore, A.D. Applehans, Rev. Sci. Instrum. 61 (1990) 607.
[18] P. Nagy, A. Skutlartz, V. Schmidt, J. Phys. B: At. Mol. Opt. Phys. 13 (1980) 1249.
[19] E. Krishnakumar, S.K. Srivastava, J. Phys. B: At. Mol. Opt. Phys. 21 (1988) 1055.
[20] E. Krishnakumar, S.K. Srivastava, Phys. Rev. A 41 (1990) 2445.
[21] P.J. Chantry, J. Chem. Phys. 51 (1969) 3369.