Production of metastable Ar^+ ions by electron-impact ionization of Ar measured by translational-energy spectroscopy

E. Y. Kamber
Department of Physics, Western Michigan University, Kalamazoo, Michigan 49008-5151

C. S. Enos and A. G. Brenton
Mass Spectrometry Research Unit, University College of Swansea, Swansea SA2 8PP, United Kingdom
(Received 13 November 1992)

The translational-energy-spectroscopy technique has been used to measure the apparent ionization-excitation functions for the metastable states $3d\,^4D$, $3d\,^4F$, $3d\,^2F$, and $3d'\,^2F$ of an Ar^+ ion beam extracted from an electron-impact ion source. The initial states were identified from the measured energy loss in the translational-energy spectra for single-electron stripping from ground-state and metastable Ar^+ ions in collisions with O_2. This technique provides an alternative method of selectivity in the study of electron-impact ionization and excitation processes.

PACS number(s): 34.50.Fa, 34.50.Pi, 34.80.Dp

I. INTRODUCTION

A great deal of attention has been paid to the study of electron-capture processes by singly charged ions and ionization processes by electron impact. Little attention has been paid, however, to the study of charge-stripping (frequently called electron-boss) processes in the low-velocity range, despite the fact that such measurements will provide a test of the applicability of various theoretical models for the removal of an electron from ions. Investigating such processes will provide important knowledge about the interaction mechanisms which is still very limited, despite substantial progress both experimentally and theoretically in the study of atomic collision processes. The interest in charge-stripping processes stems not only from fundamental aspects but also from their importance in the study of the role of impurity ions in controlled thermonuclear fusion and astrophysical plasmas. The metastability of highly excited states also has permitted the development of important techniques such as optical pumping, which can be used to produce population inversion in lasers.

The formation by electron impact of low-lying and highly excited metastable states in argon-ion beams and the determination of their fractional populations has been studied extensively by several investigators using various techniques. These techniques can be classified according to the nature of the collision experienced by the metastable ion. These include collisions with surfaces, atomic and molecular gases, photons, electrons, and interaction with electric and magnetic fields. A general method for detection of highly excited states is the neutralization method in which the yields and kinetic-energy distributions of secondary electrons emitted as a result of impact of the slow ions on a clean solid surface are measured [1–3]. For the detection of low-lying metastable ions, the main emphasis has been placed on the ion-beam-attenuation method which makes use of the different ion-current attenuations for the ground state and excited states when passing the ion beam through an appropriate gas target [4,5]. Usually, for large target thickness one of the ion components completely disappears and extrapolation of the attenuation characteristic of the other component to zero target thickness yields its fraction. Recently, state-selective single-electron-capture methods were applied to determine metastable-state fractions in multiply charged ion beams and to study the formation of the excited states formed in collisions [6–10]. More recently, Kamber, Brenton, and Hughes [11] have used translational-energy spectroscopy for the detection of long-lived highly excited Ar^{2+} ions by means of state-selective single-electron stripping processes in collisions with rare-gas atoms.

In the present work, the translational energy of the forward-scattered projectile Ar^+ ions that have undergone single-electron loss in collisions with oxygen molecules, i.e.,

$$Ar^+(3d \text{ or } nl') + O_2 \rightarrow Ar^{2+} + e + O_2 - Q \ ,$$

have been measured at an impact energy of 4 keV. In such processes the projectile loses an amount of energy (Q) that depends on the participating electronic states. With this technique we were able to study the electron-energy dependence of apparent cross sections for the production of metastable ions in an electron-impact ion source.

Data have been obtained using a double-focusing translational spectrometer based on a symmetrical arrangement of two identical cylindrical electrostatic analyzers described in detail elsewhere [12]. Briefly, the Ar^+ ions, produced in a controlled-energy electron-impact ion source, were extracted and accelerated through 4 kV. After being mass analyzed by a magnet (radius 12.5 cm), the ion passed through a cylindrical electrostatic energy monochromator (radius 38.1 cm) and a collision cell containing the low-pressure atomic target gas. Ions that had undergone electron loss were energy analyzed by scanning in tandem two postcollision electrostatic analyzers, the second of which was used to elimi-

nate low-level interferences which may be caused by ion reflections from walls and slits. The ions were then detected by an electron multiplier. The energy resolution of the primary ion beam was measured to be 0.2 eV.

II. RESULTS AND DISCUSSION

When an ion loses an electron in a collision with an atom or molecule, both the ion and atom can end up in excited states or in the ground state. Measurements of the final kinetic energy provide a characteristic energy-loss spectrum, from which the probability for each collision channel can be determined. Since most ion sources produce fractions of ions in long-lived excited states as well as in the ground state, each fraction produces its own characteristic energy-loss spectrum. Considerable advances in our understanding of the role of low-lying metastable and long-lived highly excited ions becomes possible with the use of conventional electron-impact ion sources by controlling the energy of the impacting electrons. Only recently have the crucial role and the collisional properties played by excited ions in ion-atom collisions been properly appreciated. Since excited ions are present in large abundances in plasmas, these ions must therefore be taken into account in plasma modeling. Hence, it is very important to know the fractional populations of metastable states in an ion beam, and accurate experimental data and theoretical calculations are needed for ionization cross sections of ions both in the ground state and in metastable states.

A. Translational-energy-loss spectra

Figure 1(a) shows the translational-energy-loss spectra for stripping of a single electron from 4-keV Ar^+ ions in collision with O_2 at various ionizing electron energies. Figure 1(b) displays, in an expanded energy scale, the energy-loss spectra to facilitate measurement of the relative intensities at different electron energies. The charge-stripping processes are denoted by I–X and the energies of each reaction channel are listed in Table I. In the spectrum for $E_e=31$ eV, only a single peak is observed at an energy loss of $Q\approx -29.5$ eV, which corresponds to the ionization of ground-state $(3p^5\,{}^2P)Ar^+$ accompanied by excitation of the projectile product Ar^{2+} into $3p^4\,{}^1D$ (reaction channel II). The Ar^{2+} $(3s^23p^4)$ is formed via a p-electron promotion to the continuum by the coupling of $Ar^+(3s^23p^5)+O_2$ with $Ar^{2+}(3s^23p^4)+e+O_2$.

At electron-impact energies between 32 and 38 eV, the incident singly charged ions are expected to be in the ground state as well as in the metastable states $3d$ and $3d'$. The threshold energies for Ar^+ $3d\,{}^4D,{}^4F,{}^2F,3d'\,{}^2G$, and ${}^2F$, produced by electron impact, are, respectively, 32.2, 33.4, 34.3, 34.9, and 36.1 eV. At $E_e=33$ eV, three peaks are clearly seen at $Q\approx -29.5$, -11.2, and -10 eV. The peaks at $Q\approx -10$ and -11.2 eV (the reaction channels V and VI) are, respectively, due to ionization of the metastable states $3d\,{}^4F$ and $3d\,{}^4D$ which are present in the primary Ar^+ beam, while the peak at $Q\approx -29.5$ eV is due to ionization of the $3p^5\,{}^2P$ state. The unresolved peak (IV) at around $Q=-13$ eV is due to ionization of the $(3d\,{}^4D)$ state accompanied by excitation of either the target product O_2 into the $b\,{}^1\Sigma_g$ state or the projectile project Ar^{2+} into $3p^4\,{}^1D$.

For $E_e=39$ eV, the spectrum is dominated by reaction channel VI which is due to ionization of the metastable state $(3d\,{}^4F)$, but two more peaks (VII and IX) in the spectrum are seen in addition to those observed at $E_e=33$ eV. The new peaks at $Q\approx -9$ and -7.4 eV are due to ionization of the metastable states $3d\,{}^2F$ and $3d'\,{}^2F$, respectively. There is probably a contribution from unresolved reaction channel VIII arising from the ionization of the $3d'\,{}^2G$ state of Ar^+. In our analysis, we assume that the reaction channels VI, VII, VIII, and IX are mainly due to ionization of the metastable states $3d\,{}^4F,3d\,{}^2F,3d'\,{}^2G$, and $3d'\,{}^2F$ of Ar^+. However, there can be contributions from charge-stripping processes of these states leading to the formation of excited $Ar^{2+}({}^1D)$, which they strongly overlap in the same range of Q values.

Direct evidence for the production of Ar^+ ions in highly excited metastable states has been obtained by Hagstrum [1], who studied the ejection of secondary electrons by the impact of a beam of Ar^+ on a clean molybdenum target as a function of the energy of the electron beam used to produce the ions in a Nier-type course. From his measurements, Hagstrum [1] estimated that the maximum proportion of Ar^+ ions formed in metastable states was 2%. Recently, Schweinzer and Winter [10] have incorporated a metastable ion-channel–electron-multiplier detector into a translational-energy spectrometer to study the formation of highly excited metastable Ar^+ ions by means of single-electron capture in collisions of 0.3–10-keV Ar^{2+} with Mg, Li, Na, and K. In the particular case investigated, they found that metastable Ar^+ ion-beam fractions of more than 60% were produced.

For an electron-impact energy of $E_e=50$ eV, the observed collision spectrum is again dominated by reaction channel VI due to ionization of $(3d\,{}^4F)$. However, one more peak occurs at $Q=0$ eV due to ionization of long-lived highly excited states, with excitation energies very close to the ionization potential of Ar^+ (the X channel). This reaction channel is found to occur for $E_e\geq 43$ eV

TABLE I. Single-electron stripping reaction channels of Ar^+.

	Reaction channels	Energy loss Q (eV)
I	$Ar^+(3p^5\,{}^2p)\rightarrow Ar^{2+}(3p^4\,{}^3P)$	−27.6
II	$Ar^+(3p^5\,{}^2p)\rightarrow Ar^{2+}(3p^4\,{}^1D)$	−29.34
III	$Ar^+(3p^5\,{}^2p)\rightarrow Ar^{2+}(3p^4\,{}^1S)$	−31.72
IV	$Ar^+(3d\,{}^4D)\rightarrow Ar^{2+}(3p^4\,{}^1D)$	−12.94
V	$Ar^+(3d\,{}^4D)\rightarrow Ar^{2+}(3p^4\,{}^3P)$	−11.2
VI	$Ar^+(3d\,{}^4F)\rightarrow Ar^{2+}(3p^4\,{}^3P)$	−9.97
VII	$Ar^+(3d\,{}^2F)\rightarrow Ar^{2+}(3p^4\,{}^3P)$	−9.1
VIII	$Ar^3(3d'\,{}^2G)\rightarrow Ar^{2+}(3p^4\,{}^3P)$	−8.5
IX	$Ar^+(3d'\,{}^2F)\rightarrow Ar^{2+}(3p^4\,{}^3P)$	−7.35
X	$Ar^{+**}\rightarrow Ar^{2+}(3p^4\,{}^3P)$	0

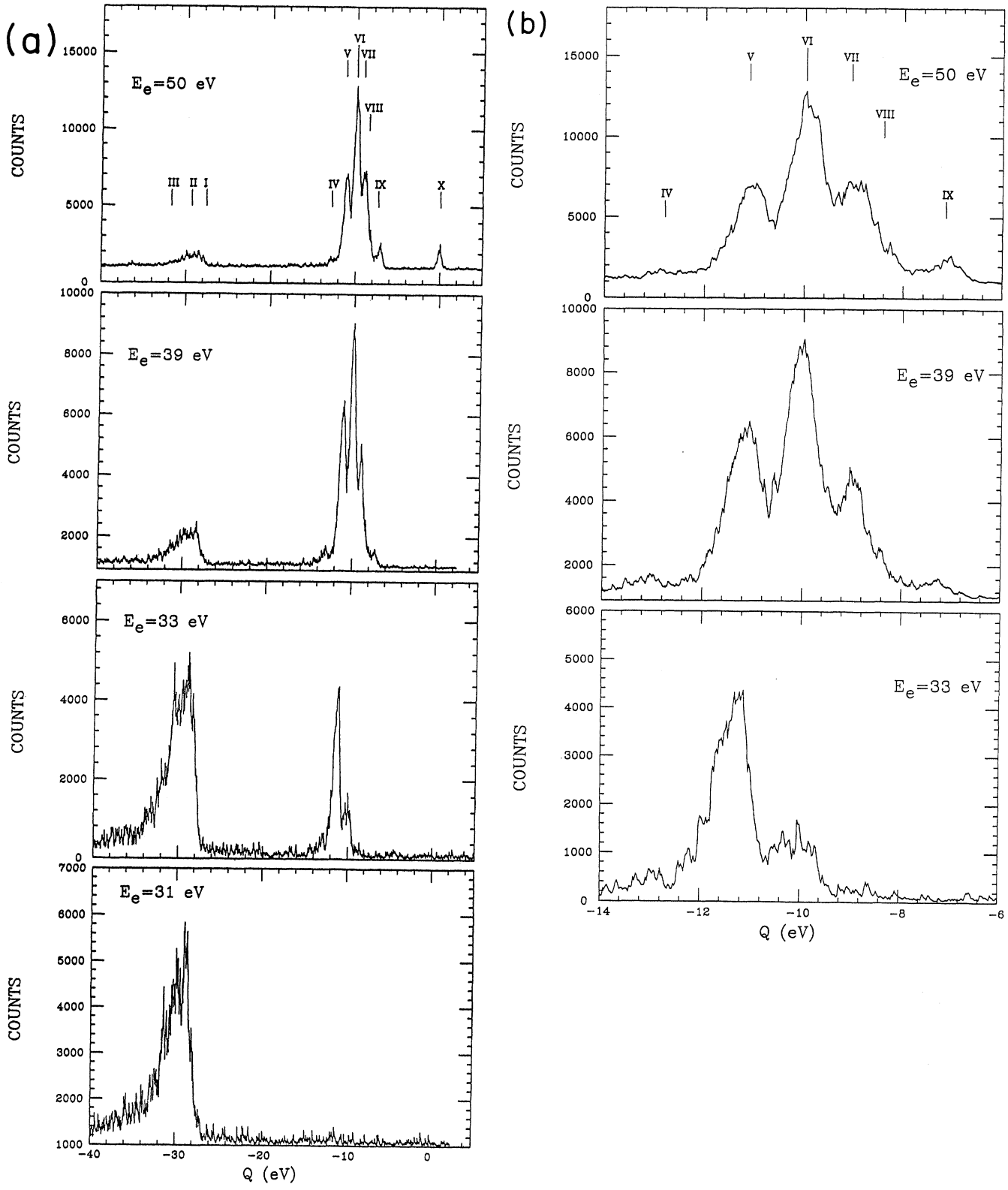

FIG. 1. Translational-energy-loss spectra for stripping of a single electron from 4-keV Ar^+ ions in collisions with O_2 at different ionizing electron energies: (a) $-40 \leq Q \leq 5$ eV; (b) $-14 \leq Q \leq -6$ eV.

and is consistent with the energy for the production of Ar^{2+}. The lifetimes of the metastable and highly excited states should be sufficiently long to survive the flight from the ion source to the collision region, since the time of flight from the source to the collision cell in the present measurements was about 8 μsec.

The formation of these metastable Ar^+ ions has also been observed by McGowen and Kerwin [13] in a mass spectrometer by means of the Aston banding technique. The energy of these metastable ions was just below the ionization threshold of Ar^{2+} and they were detected through their conversion to Ar^{2+} in the drift region of the mass spectrometer through the pressure-dependent process:

$$Ar^+ + Ar \rightarrow Ar^{2+} + Ar + e \ .$$

Direct evidence for the formation of Ar^+ and Ar^{2+} ions in autoionizing metastable states has been obtained by Daly [14]. These metastable-state ions had energies above the ionization energy of Ar^{2+}, and thus were different from those observed by Hagstrum [1] and by McGowen and Kerwin [13]. Newton, Sciamanna, and Clampitt [15] confirmed the existence of highly excited states of Ar^+ ions and showed that they undergo surface-induced transitions of the type

$$Ar^{+*} \rightarrow Ar^{2+} + e$$

at each of the various slits of the ion source. They concluded that the Ar^{2+} peak in the mass spectrum of argon was composed of two components of approximately equal intensity. One is due to a surface-induced transition at the last slit in the ion source and the other is due to autoionization of an excited Ar^+ ion after the last ion-source slit. They also showed that the excited state undergoing surface-induced transitions is a different state than that undergoing autoionization, with the autoionizing state having an energy of 0.5 ± 0.2 eV higher than the state undergoing surface-induced transitions.

B. Apparent ionization-excitation functions for the metastable Ar^+ states

We have also used the translational-energy-spectroscopy technique to study the apparent ionization-excitation functions for the $3d$ and $3d'$ states Ar^+. At each electron-impact energy the observed spectrum was used to determine the intensity for the processes corresponding to peaks V–X. The measured intensity is proportional to the product of the ionization-excitation cross section and the cross section for the stripping process, which we assume is the same for one state at different electron-impact energies. The determined functions are apparent as contributions from higher excited states cannot be excluded. Figure 2 shows the apparent ionization-excitation functions for the reaction channels V, VI, VII, IX, and X; the points were normalized to the total signal at $E_e = 44$ eV. The electron energy was calibrated from the ionization-threshold energy of Ar, and the energy scale may contain an inaccuracy of about ± 1 eV. The variation of the apparent cross section with electron energy has a characteristic form, rising from the ionization potential V_i to a maximum at an electron energy of from 1.2 to 1.8 times V_i and then decreasing. The apparent ionization-excitation functions for the production of the $3d\ ^4F$, $3d\ ^2F$, and $3d\ ^4D$ states exhibit pronounced structure in the interval 44–60 eV. The functions have a similar shape, with a sharp peak at the threshold followed by a secondary peak, and then a smooth falloff. The pronounced structures and the shoulders on the lower-energy sides of the maxima are contributions from resonance levels and the decay transitions from highly excited states to the $3d$ state. In the present work, we are considering excitation from the ground state of neutral argon to excited states of Ar^+ and we would expect all the states to be optically forbidden, because of the fact that two-electron transitions are involved; i.e., one $3p$ electron is ejected into the continuum and another $3p$ electron is promoted to an excited state [16]. The work of Varga, Hofer, and Winter [17] supports this suggestion. They concluded that the steep increase after threshold in their measurement of apparent cross sections for metastable singly charged ions is mainly due to the predominant contributions of optically forbidden transitions to the process of metastable-ion production. The double-peaked structure can also be explained as feature

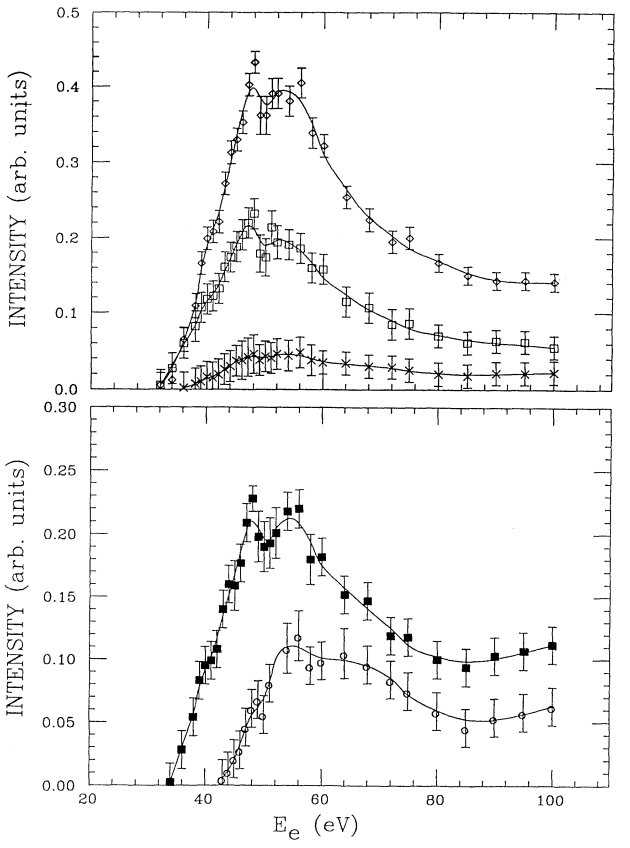

FIG. 2. Apparent ionization-excitation functions for the metastable Ar^+ states: ◇, $3d\ ^4F$; □, $3d\ ^4D$; ×, $3d'\ ^2F$; ■, $3d\ ^2F$; ○, reaction channel X. Smooth lines are drawn to guide the eye.

of the simultaneous ionization and excitation of argon and is probably associated with autoionization effects. Our curves are qualitatively similar to the cross sections for formation of metastable Ar^+ ions by electron impact observed by Hagstrum [1], Kadota and Kaneko [3], Tan and McConkey [16], Varga, Hofer, and Winter [17], and Rosner, Gaily, and Holt [18].

III. CONCLUSION

In this study we have reported measurements of single-electron stripping in Ar^+-O_2 collisions at an impact energy of 4 keV by means of translational-energy spectroscopy. These results show that the dominant reaction channels are due to ionization of metastable $Ar^+(3d)$ states. The variation of the observed spectrum for Ar^{2+} production merely reflects the increasing fraction of metastable and highly excited states in the Ar^+ ion beam as the electron-impact energy is increased. We have used O_2 as a collision target since the translational-energy-loss spectra for stripping of a single electron from Ar^+ ions in collision with O_2 reveal five resolved peaks, whereas with the targets He and Ar as collision gases, the spectra show only one broad peak within the same range of Q values. The differences in the spectra due to nature of the targets and the effects of the ejected electron will be discussed in more detail in a forthcoming publication. Finally, we have also measured the apparent ionization-excitation functions for the $3d$ and $3d'$ states of Ar^+. These data can be of interest to plasma studies where they can be used to estimate the influence of long-lived excited states on charge balance.

ACKNOWLEDGMENTS

E.Y.K. wishes to express his gratitude for the kind hospitality extended to him during his stay at the University College of Swansea, where part of this work was performed. This work was supported in part by NATO collaborative research Grant No. CRG. 920243.

[1] H. D. Hagstrum, Phys. Rev. **104**, 309 (1956).
[2] P. Varga and H. Winter, Phys. Rev. A **18**, 2453 (1978).
[3] K. Kadota and Y. Kaneko, J. Phys. Soc. Jpn. **38**, 524 (1975).
[4] B. R. Turner, J. A. Rutherford, and D. M. J. Compton, J. Chem. Phys. **48**, 602 (1968).
[5] M. Vujovic, M. Matic, B. Corbic, and Yu. S. Gordeev, J. Phys. B **5**, 2085 (1972).
[6] A. Matsumoto, S. Ohtani, and T. Iwai, J. Phys. B **15**, 1871 (1982).
[7] A. Brazuk and H. Winter, J. Phys. B **15**, 2233 (1982).
[8] B. A. Huber and H-J. Kahlert, J. Phys. B **16**, 4655 (1983).
[9] A. Brazuk, D. Dijkkamp, A. G. Drentje, F. J. de Heer, and H. Winter, J. Phys. B **17**, 2489 (1984).
[10] J. Schweinzer and H. Winter, J. Phys. B **22**, 893 (1989),
[11] E. Y. Kamber, A. G. Brenton, and S. Hughes, J. Phys. B **23**, L311 (1990).
[12] P. Jonathan, M. Hamdan, A. G. Brenton, and G. D. Willett, Chem. Phys. **119**, 159 (1988).
[13] J. W. M. McGowan and L. Kerwin, Can. J. Phys. **41**, 1535 (1963).
[14] N. R. Daly, Proc. Phys. Soc. London **85**, 897 (1965).
[15] A. S. Newton, A. F. Sciamanna, and R. Clampitt, J. Chem. Phys. **46**, 1779 (1967).
[16] K-H. Tan and J. W. McConkey, Phys. Rev. A **10**, 1212 (1974).
[17] P. Varga, W. Hofer, and H. Winter, J. Phys. B **14**, 1341 (1981).
[18] S. D. Rosner, T. D. Gaily, and R. A. Holt, J. Phys. B **9**, L489 (1976).