

## Excitation of Electronic States of Ar, H<sub>2</sub>, and N<sub>2</sub> by Positron Impact

J. P. Sullivan, J. P. Marler, S. J. Gilbert, S. J. Buckman,\* and C. M. Surko

*Department of Physics, University of California, San Diego, California 92093-0319*

(Received 27 March 2001; published 25 July 2001)

We have measured the first state-resolved, absolute cross sections for positron excitation of electronic states of an atom or molecule using a high resolution ( $\Delta E \sim 25$  meV FWHM) beam of positrons from a Penning-Malmberg trap. We present cross sections for the excitation of the low-lying levels of Ar, H<sub>2</sub>, and N<sub>2</sub> for incident positron energies between threshold and 30 eV. For Ar and H<sub>2</sub>, comparison can be made with theoretical calculations, and, in the case of H<sub>2</sub>, the results resolve a significant discrepancy between the only two available calculations.

DOI: 10.1103/PhysRevLett.87.073201

PACS numbers: 34.85.+x, 34.50.Fa, 34.50.Gb

An accurate knowledge of cross sections for positron impact excitation of electronic states of atoms and molecules is important in a number of fundamental and applied areas. It is now well known that an accurate theoretical description of positron collisions requires substantially more than simply changing the sign of the projectile and dropping the exchange interaction from established electron scattering calculations. One must, for example, consider the details of the short-range polarization and correlation effects, which are different from electron scattering, and, in the case of higher energy impacts, include the role of positronium formation, a channel which is not present for electron scattering. Cross sections for excitation of atoms and molecules by positrons are also required in processes such as condensed matter applications [1] and to understand the collisional accumulation and cooling of positrons in buffer-gas traps [2].

The observation and absolute measurement of electronic excitation of atoms or molecules by positron impact have been rare. For the most part this is due to the significant experimental difficulty involved in obtaining bright, monochromatic beams of positrons. The low fluxes and broad energy widths ( $\sim 0.5$  eV) obtained in most conventional positron beam experiments has meant that only a few measurements of electronic excitation have been attempted in the rare gases [3–5] and for O<sub>2</sub> [6]. The energy widths of the beams used in these pioneering investigations meant that the study of discrete excited states was not possible. In the case of the rare gases, cross sections for either a complete manifold of excited states or for all bound levels were achieved.

Recent advances in positron accumulation using buffer-gas traps [2] and new developments in trap-based beams [7] means that high resolution, state-resolved collision studies of atoms and vibrationally resolved studies of molecules are now realizable. This was recently demonstrated for the near-threshold vibrational excitation of a number of simple molecules [8,9]. In this Letter, we used such an accumulator, and an apparatus for low energy collision studies, to measure absolute collision cross sections for selected electronic excited states of Ar, H<sub>2</sub>, and N<sub>2</sub>. In argon we studied the  $3p^5(^2P_{3/2})4s$

( $J = 1$ ) and  $3p^5(^2P_{1/2})4s$  ( $J = 1$ ) levels (where  $J$  is the total angular momentum) which have threshold energies of 11.63 and 11.82 eV, respectively. In H<sub>2</sub>, cross sections for the lowest excited singlet state, the  $B^1\Sigma$  state, which has an excitation threshold of 11.19 eV, have been measured. For N<sub>2</sub>, we measured cross sections for the  $a^1\Sigma$  and  $a^1\Pi$  states which have their excitation thresholds at 8.399 and 8.549 eV, respectively. For Ar and H<sub>2</sub> the present measurements extend from near the thresholds of the excited states to 30 eV, while for N<sub>2</sub> the maximum energy is 20 eV.

Theoretical studies of electronic excitation processes by positron impact have also been limited, although a variety of close-coupling (CC), distorted wave, polarized orbital, and random phase approximations were used for calculations on atomic systems. In particular, for argon there have been distorted-wave calculations, in an  $LS$  coupling basis, of the  $n^1P$  levels ( $n = 3-6$ ) [10]. Note that the use of terms such as  $^1P$  for the excited states in argon is not strictly correct as it is best described by a coupling scheme intermediate between  $LS$  and  $jj$ . The sum of these cross sections is in reasonable accord with the early unresolved measurements of electronic excitation [3–5].

For molecules, the only contemporary theoretical calculations are for H<sub>2</sub>, where close-coupling [11] and Schwinger variational [12] calculations were carried out at energies from near threshold to about 80 eV. One notable aspect of these calculations is that they yield cross sections that differ by a factor of 5 to 10 in absolute magnitudes.

Our experiments are carried out using a buffer-gas accumulator for the production of a cold positron beam [2,7]. The pulsed beam consists of about  $2-3 \times 10^4$  positrons, in a pulse of  $< 2 \mu s$  width with a repetition rate of  $\sim 4$  Hz, and has an energy width which is typically 25–30 meV (FWHM). After their release from the accumulator, the positrons are guided through a scattering cell containing the gas of interest and a retarding potential analyzer (RPA) by a magnetic field of up to 0.1 T. The gas cell has a length of 38.1 cm. The absolute number density of the target gas that it contains is measured with a capacitance manometer. Positrons that are transmitted by the RPA annihilate on a plate, and

the resultant  $\gamma$  rays are detected by a NaI scintillation detector.

The details of the experimental technique for the scattering measurements are contained in several recent publications [7–9] so only a brief summary is given here. Both the positron scattering in the gas cell and the subsequent analysis in the RPA take place in a magnetic field. The positron energy in the magnetic field,  $E_T$ , can be divided into two components,  $E_\perp$  and  $E_\parallel$ , with  $E_T = E_\perp + E_\parallel$ , where  $E_\parallel$  is the energy in the motion parallel to the magnetic field and  $E_\perp$  is the energy in the particle's gyromotion perpendicular to the field. When a positron undergoes an inelastic collision, the total energy of the scattered positron is given by  $E_S = E_T - E_{\text{ex}}$ , where  $E_{\text{ex}}$  is the excitation energy of the state. Since the RPA analyzes only  $E_\parallel$ , it is difficult to separate changes in  $E_\parallel$  due to the particle scattering at an angle to the field (which occurs for both elastic and inelastic scattering) from changes in  $E_T$ . However, by arranging the analysis of  $E_\parallel$  to take place in a magnetic field a factor of  $M$  lower than in the scattering region, we are able to exploit the adiabatic properties of the positron's motion in a slowly varying magnetic field (i.e.,  $E_\perp/B = \text{const}$ ) to convert all but a fraction  $1/M$  of  $E_\perp$  to  $E_\parallel$ . In this case, the RPA measurement provides a good measure of  $E_T$ , and the energy loss process produces a clearly resolvable “step” in the RPA curve at a voltage, corresponding to  $E_{\text{ex}}/e$  from the beam cutoff voltage. In the experiments reported here,  $M \sim 35$ . For argon, two such steps are observed corresponding to the excited  $4s$  states, separated by  $\sim 200$  meV. For the molecular excitations a series of steps are observed, spread over a broad energy range, due to the manifold of vibrational levels in the electronic states.

An example of an RPA response curve illustrating the effect of electronic excitation is shown in Fig. 1 for scattering from  $\text{N}_2$  at an incident energy of 11 eV. One way to view this spectrum is as the integral form of a conventional energy loss spectrum. Thus the peaks which would arise due to an excitation process in a conventional spectrum appear as downward steps in the RPA transmission curve. In the energy loss region corresponding to the excitation of the  $a^1\Sigma$  and  $a^1\Pi$  states, there is an overall broad step between 8.5 and 10.5 eV due to the excitation of the vibrational manifolds of both states. The smaller steps correspond to the excitation of the individual vibrational levels, the positions of which are indicated by vertical bars in the plot. At lower energy loss the excitation is mainly due to the  $a^1\Pi$  state, because of the Franck-Condon factors for the two states, while, at higher values, both states contribute. Each RPA curve is fit by an expression consisting of a series of summed error functions representing the energetically accessible vibrational levels. The energy of each step is given by known spectroscopic values, while the relative magnitudes of the steps within each excited-state manifold are fixed according to the known Franck-Condon factors for these

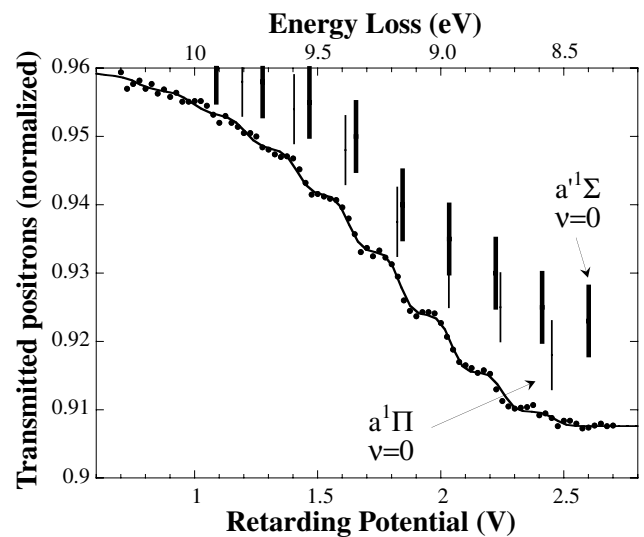


FIG. 1. RPA data for the excitation of  $\text{N}_2$  by 11 eV positrons. The transmitted signal is normalized to the incident beam strength and the vertical bars represent the vibrational energy levels of the  $a^1\Sigma$  and  $a^1\Pi$  states. The solid line is a least-squares fit to the data (see text) with a reduced chi-squared parameter of 1.57.

transitions. The solid line in the figure is an example of such a fit.

For each target, the magnitudes of the steps in the RPA curve are proportional to the electronic excitation cross sections. The method of calculating the absolute cross section was described previously [7–9]. For argon, the calculation of the cross section is relatively straightforward. For the molecules, however, while the cross sections are still governed by the step sizes, consideration has to be given to the overlap of any nearby states and the Franck-Condon factors for the excitations. These considerations are discussed later. The uncertainties in the integral cross sections vary between 5% and 20%. This is predominantly due to statistical errors, with systematic effects from factors such as the uncertainties in pressure measurement and effective scattering cell length also included.

In Fig. 2 we show the measured cross sections for the two excited  $4s$  ( $J = 1$ ) states of argon. The cross sections are small, but similar in magnitude to their electron scattering counterparts [13]. The cross section for the  $1/2$  core level is larger in magnitude across the entire energy range studied. This is consistent with the  $1/2$  core state being more singlet in nature than the  $3/2$  core state. At energies between 15–20 eV both cross sections decrease in magnitude, which may be associated with the relatively strong onset of ionization at 15.43 eV.

In Fig. 3 we show the sum of the cross sections for the two  $4s$  ( $J = 1$ ) states and make a comparison with two previous measurements [4,5]. The previous measurements were for all excited states, and thus one would expect that their magnitude would be larger than the present data, which is generally what is observed. One data set

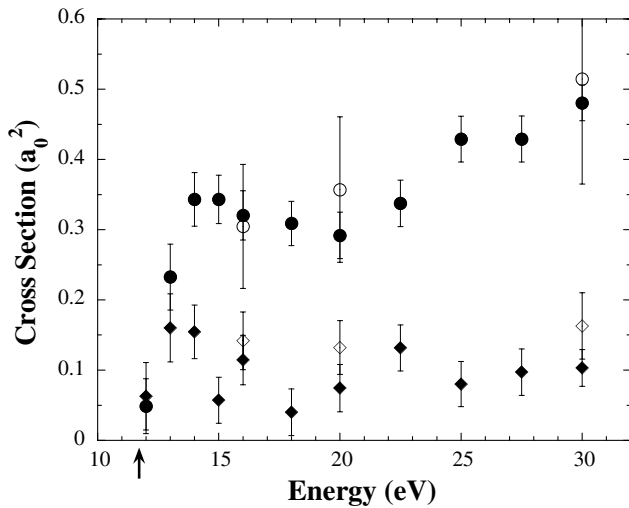


FIG. 2. Integral cross sections for the excitation of the  $3p^5(^2P_{3/2,1/2})4s$  states of Ar by positron impact; (●, ○) 1/2 state, (◆, ◇) 3/2 state. In each case the closed symbols are the present positron data, and the open symbols are the electron scattering data of Ref. [13]. The arrow indicates the position of the excitation thresholds.

[5] has been scaled by 0.6 in order to fit it to the plot. The previous data indicate quite strong upward steps in the cross section near the ionization threshold. This is not observed in the present measurements and is most likely due to the difficulty of discrimination between ionization and excitation in the previous experiments. The uncertainties in the present state-selected cross sections are considerably smaller than those for previous measurements and thus they provide a substantially improved base for comparison with theory. Such a comparison is made in Fig. 3 with a distorted wave calculation [10] for the  $4s^1P$  state. This  $LS$ -coupling calculation provides a reasonable estimate of the magnitude of the summed cross section

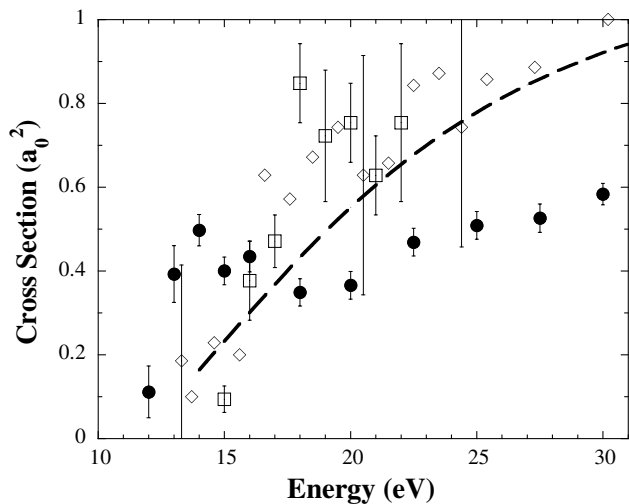


FIG. 3. Integral cross section for the sum of the two  $4s$  ( $J = 1$ ) states of Ar. (●) present data, (□) Ref. [4], (◇) Ref. [5] scaled by 0.6, and (---) the theoretical result of Ref. [10].

at about 17 eV, but does not reproduce the near-threshold peak seen in the experimental data. At 30 eV the theory is about 50% higher than the experiment.

The cross section for the  $B^1\Sigma$  state of  $H_2$  is shown in Fig. 4. The excitation of the vibrational manifold of this state can be measured unambiguously up to an energy loss of about 12.3 eV (i.e., to  $\nu = 6$ ), at which point other excited channels, but principally the  $C^1\Pi$  state, are open. By using Franck-Condon factors from the literature [14], we can calculate the integral cross section for the  $B$  state with the measured step corresponding to  $\sim 37\%$  of the full integral cross section, when all vibrational channels are open. As shown in Fig. 4 the cross section for the  $B$  state rises relatively slowly from threshold to a maximum value of about  $1.5a_0^2$  near 20 eV. Between threshold and 30 eV this cross section is larger than that for electron impact [14]. Also shown in Fig. 4 are two theoretical calculations for this process, one a close-coupling approach [11] and the other using the Schwinger multichannel (SMC) theory [12]. The present measurements are in reasonably good agreement with the two-state SMC calculation, which, in turn, places them a factor of 5–10 below the CC cross section. The reasons for this discrepancy between the calculations are not understood although several possibilities have been discussed [12]. Our experiments clearly favor the SMC calculation.

Finally, in Fig. 5 we show cross sections for the excitation of the  $a^1\Sigma$  and  $a^1\Pi$  states of  $N_2$  at energies up to 20 eV. In this case, as illustrated in Fig. 1, the cross sections for the two states are extracted by fitting the RPA curve with the sum of a number of error functions. We note that the inclusion of a third state in this energy region, the  $w^1\Delta$  state which has a threshold energy of 8.89 eV, does not improve the quality of the fit, leading us to conclude that its cross section is significantly smaller. Unfortunately,

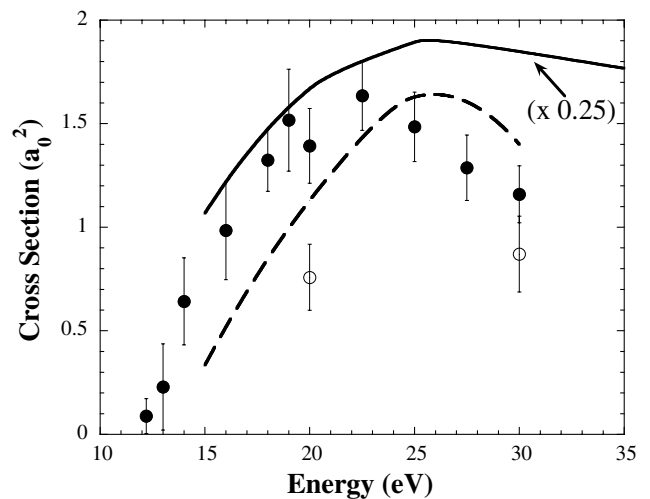


FIG. 4. Integral cross section for the excitation of the  $B^1\Sigma$  state of  $H_2$ . (●) present data, (○) electron data from Ref. [14], (---) calculation from Ref. [11] scaled by 0.25, and (—) calculation from Ref. [12].

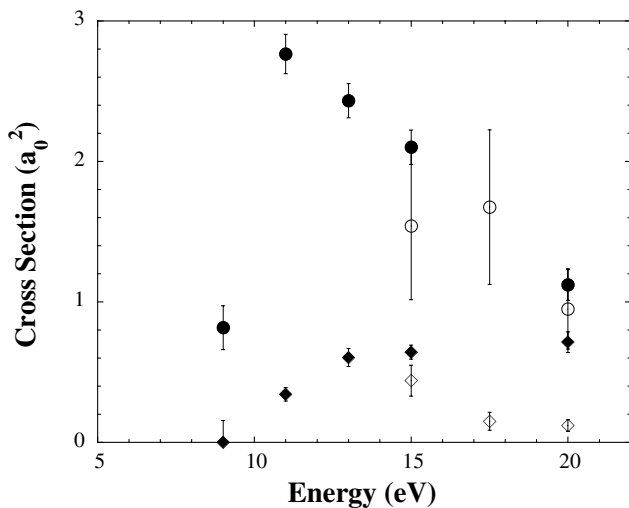


FIG. 5. Integral cross sections for the (●, ○)  $a^1\Pi$  and (◆, ◇)  $a^1\Sigma$  states of  $N_2$ . The closed symbols are the present positron data, and the open symbols are for electron impact from Ref. [15].

there are no theoretical estimates for any of these cross sections with which we can compare. For both states the near-threshold cross sections are larger by about a factor of 2 than their electron counterparts [15]. The  $a$ -state cross section also appears to rise steeply at threshold, and this warrants closer investigation.

It is interesting to note that we see no evidence in the argon data for the excitation (from the singlet ground states) of states which are largely triplet in character. In particular the remaining levels in the  $4s$  manifold, the  $3p^5(^2P_{3/2})4s$  ( $J = 2$ ) and  $3p^5(^2P_{1/2})4s$  ( $J = 0$ ) levels at 11.55 and 11.72 eV, respectively, are not observed. These states are both metastable and are readily excited by near-threshold electron impact. In  $H_2$  there are also a number of triplet states (e.g.,  $c^3\Pi$  and  $a^3\Sigma$ ) near the  $B^1\Sigma$  state, but there is no evidence for their excitation at any of the energies studied here. This observation is not surprising but, to our knowledge, it is the first such experimental determination for positron scattering. In the absence of the exchange interaction the only other possible spin-flip mechanism, the spin-orbit interaction, is unlikely for the targets studied because of their relatively low atomic number and the repulsive nature of the static Coulomb potential.

The work described here further illustrates the unique advantages to be gained from the cold, bright positron beams obtained using positron-buffer gas trapping and scattering studies exploiting magnetized-beam techniques. Measurements with such high energy resolution and sensitivity are not achievable with conventional positron

sources. The integral cross sections presented here provide benchmark data for comparison with, and further development of, positron scattering theory for excitation processes in both atoms and molecules. The comparison with electron scattering cross sections also provides interesting insights. For example, in  $N_2$  there is strong, near-threshold enhancement of the  $a^1\Pi$  state for positron impact not seen in electron scattering. The data highlight the quality of the positron measurements relative to those available in the literature for electron scattering (i.e., the latter obtained by extrapolating and integrating differential cross sections). Thus the direct technique of measuring integral inelastic cross sections described here can also be expected to be of interest in the electron scattering community.

This work is supported by the National Science Foundation and the Office of Naval Research. We acknowledge the expert technical assistance of Gene Jerzewski. S. J. B. acknowledges the support of the Fulbright Foundation and the University of California, San Diego. We thank Michael Brunger and Bob McEachran for many useful conversations and for providing tabulated data.

---

\*Permanent address: Australian National University, Canberra, ACT, Australia.

- [1] P. J. Schultz and K. G. Lynn, *Rev. Mod. Phys.* **60**, 701 (1988).
- [2] S. J. Gilbert, C. Kurz, R. G. Greaves, and C. M. Surko, *Appl. Phys. Lett.* **70**, 1944 (1997).
- [3] O. Sueoka, *J. Phys. Soc. Jpn.* **51**, 3757 (1982).
- [4] P. G. Coleman, J. T. Hutton, D. R. Cook, and C. A. Chandler, *Can. J. Phys.* **60**, 584 (1982).
- [5] S. Mori and O. Sueoka, *J. Phys. B* **27**, 4349 (1994).
- [6] Y. Katayama, O. Sueoka, and S. Mori, *J. Phys. B* **20**, 1645 (1987).
- [7] S. Gilbert, J. Sullivan, R. Greaves, and C. Surko, *Nucl. Instrum. Methods Phys. Res., Sect. B* **171**, 81 (2000).
- [8] S. J. Gilbert, R. G. Greaves, and C. M. Surko, *Phys. Rev. Lett.* **82**, 5032 (1999).
- [9] J. P. Sullivan, S. J. Gilbert, and C. Surko, *Phys. Rev. Lett.* **86**, 1494 (2001).
- [10] L. A. Parcell, R. P. McEachran, and A. Stauffer, *Nucl. Instrum. Methods Phys. Res., Sect. B* **171**, 113 (2000).
- [11] T. Mukherjee, S. Sur, and A. Gosh, *J. Phys. B* **24**, 1449 (1991).
- [12] J. L. S. Lino, J. S. E. Germano, and M. A. P. Lima, *J. Phys. B* **27**, 1881 (1994).
- [13] A. Chutjian and D. C. Cartwright, *Phys. Rev. A* **23**, 2178 (1981).
- [14] M. Khakoo and S. Trajmar, *Phys. Rev. A* **34**, 146 (1986).
- [15] L. Campbell *et al.*, *J. Phys. B* **34**, 1185 (2001).