Relative Charge-Transfer Efficiencies of $^2P_{3/2}$ and $^2P_{1/2}$ Xenon Ions in Xe and in O_2

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We have shown that the concentration of Xe^+ $^2P_{3/2}$ ions formed in an electron-impact ion source may be monitored by utilizing near-resonant charge transfer of Xe^+ beams with molecular oxygen. This measurement provides a means of assaying the fraction of excited ions in the Xe^+ beam and affords a technique for studying the effects of fine structure on the symmetric charge-transfer process: $Xe^+ + Xe \rightarrow Xe + Xe^+$. With 25-eV electrons, we find that the Xe^+ beam is about 80% $^2P_{3/2}$ state, while the remaining 20% appears to be principally $^2P_{1/2}$. The charge-transfer cross section for the excited component in xenon was found to be 1.0 ± 0.15 relative to that of the $^2P_{3/2}$ ion, over a large range of incident ion energy.

I. INTRODUCTION

OF recent concern is the importance of fine structure in symmetric charge-transferring collisions involving the noble gases. That there might be a marked difference in the two symmetric processes

$$Ar^+(^2P_{3/2}) + Ar \rightarrow Ar + Ar^+ \quad (1)$$

and

$$Ar^+(^2P_{1/2}) + Ar \rightarrow Ar + Ar^+ \quad (2)$$

was first proposed by Gilbody and Hasted[1] as a means of explaining their observation of a nonresonant behavior in the $_{10}\sigma_{01}$ cross section for argon as a function of ion energy. Since for this species the fine-structure separation is only 0.18 eV, one might expect that such a behavior could be even more pronounced for the heavier noble gases. Subsequent work by McGowan and Kerwin[2] and by Hussain and Kerwin[3] suggests that the ratio of the two cross sections $\sigma(J=\frac{1}{2})/\sigma(J=\frac{3}{2})$ for the case of argon at 1 keV is approximately 1.3, while for the case of krypton, $\sigma(J=\frac{3}{2})$ appears considerably larger than $\sigma(J=\frac{1}{2})$, perhaps by a factor of 2.

A major uncertainty in such measurements lies in determining the concentration of the higher $J=\frac{1}{2}$ state of the ion in question as a function of ionizing electron energy. Ionization efficiency (IE) curves often show considerable structure, generally attributed to autoionizing states in the atom,[4] although the results are not generally consistent.[5] Also, when ion-source operating pressures are high, collisional deactivation could reduce the population of the $^2P_{1/2}$ state.

In this work, our objective was to establish the sensitivity of the symmetric charge-exchange cross section for Xe ions incident on Xe to the electron-impact energy used in forming the ions. However, to make the results meaningful, a method was required whereby the relative population of the two fine-structure states could be assayed independently from IE curves. To this end, we have utilized the near-resonant process

$$Xe^+(^2P_{3/2}) + O_2 \rightarrow Xe + O_2^+(v), \quad (3)$$

which has an energy defect of $12.13 - 12.07 = 0.06$ eV for O_2^+ ions formed with $v=0$. Now, the first excited electronic state of O_2^+ lies at 16.8 eV, so that there is no such state which is closely resonant with the $^2P_{1/2}$ state at Xe^+ at 13.43 eV. Therefore, at low incident ion energies the charge-exchange process for this system should be almost entirely due to the $^2P_{3/2}$ state. As the electron-impact energy is increased, the cross section should decrease in proportion to the excited ion concentration.

II. PROCEDURE

A. $Xe^+ + O_2$ Measurement

Because of the large energy separation of the two fine-structure states in xenon, it is possible to obtain an adequate beam of ions using electron energies at or just below the appearance potential for the $J=\frac{1}{2}$ state. The apparatus, described in earlier work,[6] employs an ion source in which the pressure may be reduced to a few microns, and electron energies may be varied continuously from threshold to 50 eV or higher. Electron energy spread is approximately 0.5 eV. In this work, the electron energy was varied from 13 to 30 eV, and the ion beam energy was varied from 50 to 1000 eV. The charge-transfer cell consists of a cylindrical grid surrounded by a concentric cup. As the potential of the cup is raised, slow ions formed by charge exchange are collected on the grid.[6]

In Fig. 1 we have plotted the slow-ion current to the grid as a function of cup potential for the case of Xe^+

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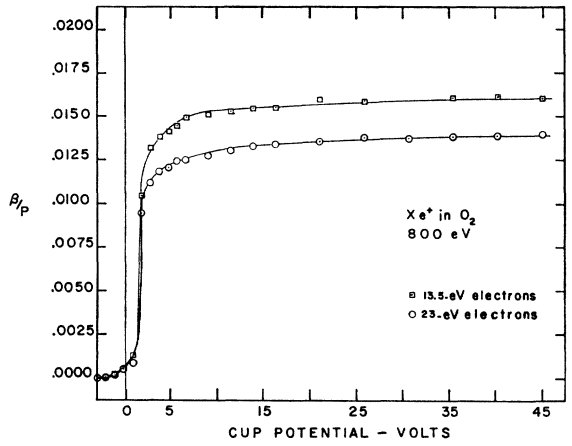

FIG. 1. Curves of slow-ion current versus cup potential for Xe^+ in O_2 at 800-eV ion energy, illustrating the sensitivity to ionizing electron energy.

ions passing through oxygen at a beam energy of 800 eV. The higher curve was obtained using 13.5-V ionizing electrons, while the lower curve is that obtained with 23-V electrons. For the ordinate we use β/P, where β is the slow-ion current formed in the transfer cell divided by the incident ion current, and P is the pressure of the oxygen target. The difference in the heights of the two curves indicates a fractional reduction of the $^2P_{3/2}$-state concentration by at least 16% when 23-eV electrons are used. By holding the cup potential constant at +5 V and varying the ionizing electron energy, the data shown in Fig. 2 are obtained. This is illustrated for beam energies of 200 and 800 eV. Over-all decreases in the slow-ion current are found to be 23 and 18%, respectively. The larger value is probably more correct since, at 800 eV, some contribution may be expected from the $Xe^+(^2P_{1/2})+O_2$ charge-transfer process. A reduction of 23% was also obtained with a 100-eV beam. Because of instrumental uncertainties in the relative measurements, some of which may be due to small pressure variations, we conclude that at 30-eV electron energy, the Xe^+ beam consists of (77 ± 3)% ground-state ions.

In this work the target pressure was maintained at approximately 0.25 mTorr. It was monitored continuously by an MKS capacitance manometer and also measured periodically by a McLeod gauge. The ion source was operated at a pressure of 4 mTorr, although a pressure of 16 mTorr was found to yield similar results.

That the excited ions are predominantly in the $^2P_{1/2}$ state is suggested by the general shape of the two experimental curves in Fig. 2. Most of the decrease in β/P occurs below 20 eV, and there are no other metastable states of Xe^+ in this interval. It is of interest to compare the changes in the observed beam composition with those inferred from the ionization efficiency curves for xenon recently obtained by Winters, Collins, and Courchene,[5] under the assumption that the plot remains linear at higher electron energies. At the bottom of Fig. 2, we have plotted the fraction f of $^2P_{3/2}$ ions as a function of ionizing electron energy ϵ, given by the ratio

$$f=\frac{\epsilon-\epsilon_1}{m_2/m_1(\epsilon-\epsilon_2)+(\epsilon_2-\epsilon_1)}, \quad \epsilon\geq\epsilon_2. \tag{4}$$

Here, ϵ_1 and ϵ_2 are the ionization potentials of the lower $(J=\frac{3}{2})$ and higher $(J=\frac{1}{2})$ state; m_1 is the slope of the IE curve for $\epsilon_1<\epsilon<\epsilon_2$, and m_2 is that for $\epsilon>\epsilon_2$. Approximately 83% is suggested by this procedure as a limiting value of $^2P_{3/2}$ ion concentration,[7] including the auto-

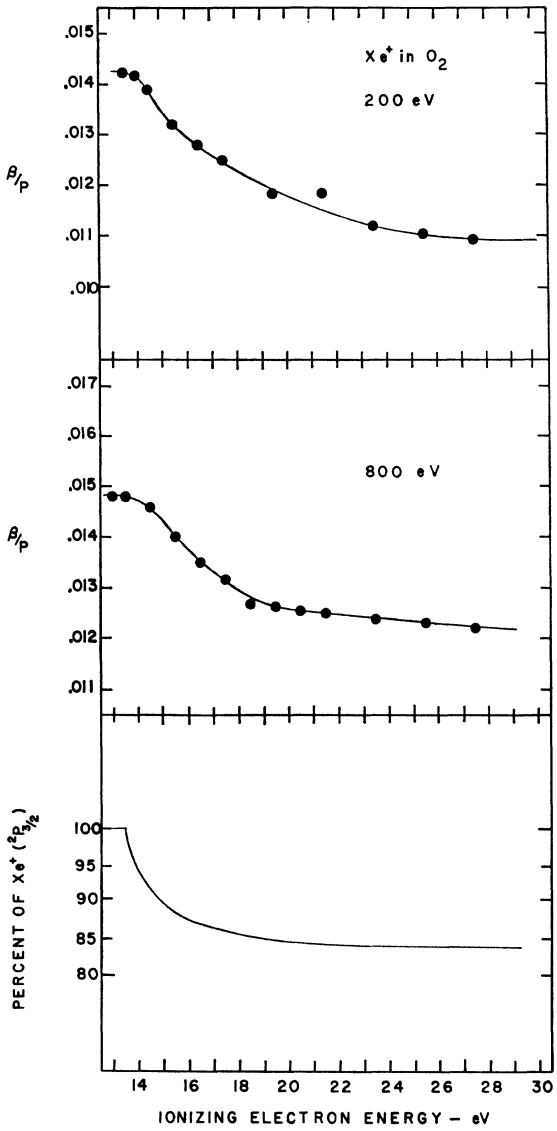

FIG. 2. Top and center: Observed decreases of O_2^+ slow-ion current with increasing ionizing electron energy. Bottom: Decrease in concentration of $^2P_{3/2}$ ions according to Eq. (4).

[7] Similar treatment of Clarke's older measurements [E. M. Clarke, Can. J. Phys. 32 (1954)] gives ~70% concentration.

ionizing contribution. Again, most of the decrease occurs for electron energies less than 20 eV.

B. $Xe^+ + Xe$ Measurement

By varying the electron energy over the same interval, we may now see what effect this increasing concentration of $J=\frac{1}{2}$ ions has on the symmetric process:

$$Xe^+ + Xe \rightarrow Xe + Xe^+. \quad (5)$$

As seen in Fig. 3, this cross section is found to be insensitive to the ionizing electron energy, over a wide range of ion beam energy. Variations with electron energy are no greater than about $\pm 3\%$. With the observed beam composition, this result places a value on the ratio $\sigma(J=\frac{3}{2})/\sigma(J=\frac{1}{2})$ of 1.0 ± 0.15. Application of the Firsov[8] formula to the two resonant processes represented by Eq. (5) gives a ratio of approximately 1.1. This is illustrated in Fig. 4, in which we have also plotted our experimental cross sections as a function of energy. Agreement with the Firsov formula for $J=\frac{3}{2}$ is quite good. The experimental results of Dillon *et al.*,[9] and of Kushnir *et al.*,[10] are also plotted. The theoretical calculation by Rapp and Francis[11] agrees closely with the lower of the two Firsov curves.

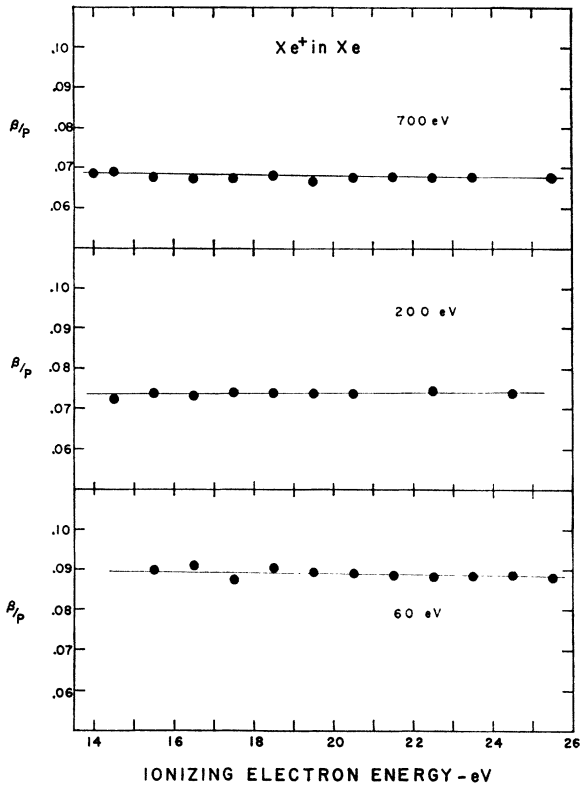

FIG. 3. Effect of varying ionizing electron energy on the symmetric $Xe^+ + Xe$ charge-exchange cross section.

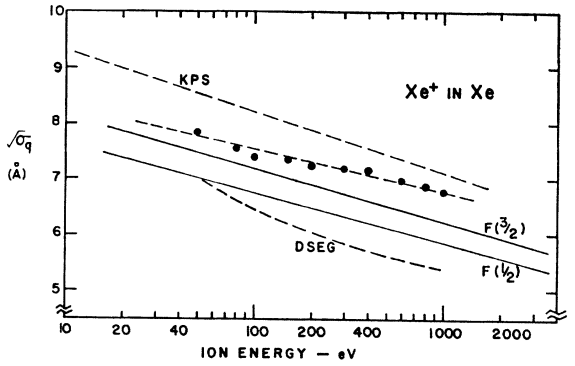

FIG. 4. Symmetric charge-transfer cross section for xenon ions in xenon as a function of beam energy. ●: this work; $F(\frac{3}{2})$ and $F(\frac{1}{2})$: cross sections calculated with Firsov formula assuming resonant $\frac{3}{2}\rightarrow\frac{3}{2}$ processes, respectively; DSEG: measured results (Ref. 9); KPS: measured results (Ref. 10).

III. CONCLUSIONS

The large fine-structure splitting of the Xe^+ ion, together with the near-resonant behavior of the $Xe^+(^2P_{3/2})+O_2$ reaction, provides a means for assaying the Xe^+ ion beam composition. At 25-eV ionizing electron energy, the beam was found to consist of about 80% $^2P_{3/2}$ ions, which is comparable to that inferred from extrapolation of the IE curve for xenon. At the higher electron energies, the decay of other excited species could affect our observed composition.

In contrast to the O_2-target case, the symmetric charge-transfer cross section shows no pronounced sensitivity to the beam composition, and we conclude that the two fine-structure states undergo charge transfer in xenon with nearly the same efficiency. This result differs from that obtained by other investigators for argon and krypton, but is in accord with the Firsov theory for symmetric resonant charge transfer. The measured symmetric cross section for xenon is within 20% of the Firsov calculation for the $\frac{3}{2}\rightarrow\frac{3}{2}$ process over the energy range of 50 to 1000 eV, although the energy dependence appears to be somewhat less than the theoretical result.

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