Investigation of the Wigner Spin Rule in Collisions of N^+ with He, Ne, Ar, N_2, and O_2†

John H. Moore, Jr.
Chemistry Department, University of Maryland, College Park, Maryland 20742
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The Wigner electron-spin-conservation rule has been investigated in collisions of 1.5–3.5-keV N^+ with He, Ne, Ar, N_2, and O_2 by the technique of ion-impact energy-loss spectrometry. Inelastic and superelastic collisions involving both ground-state and metastable N^+ have been observed in the energy-loss spectrum between −2.1 and 4.1 eV. The intensities of many of these transitions have been measured and the beam composition and transition cross sections have been determined. In collisions of N^+ with the singlet-state targets, spin-conservative transitions are nearly three orders of magnitude more probable than spin-nonconservative transitions. In the N^+-O_2 collisions there is some evidence that the Wigner rule does not hold as well as in less complex collisions.

INTRODUCTION

The Wigner spin-conservation rule requires that the total electron-spin angular momentum of a pair of atoms or molecules does not change in the course of a collision.[1] This paper reports an investigation of the validity of this rule in the case of inelastic collisions of a few keV energy between N^+ and various atoms and molecules.

Massey and Burhop state the Wigner rule in the following manner.[2] Two ions, atoms or molecules with initial electron-spin quantum numbers s_1 and s_2 possess a total-spin angular momentum $\vec{S}$ which is the vector sum of the spins of the individual systems. The resultant total-spin quantum number is

$$S=|\vec{S}|=(s_1+s_2), \ldots, |s_1-s_2| .$$

Assuming very-weak coupling between electron-spin and orbital angular momentum during a collision, the Wigner rule states that the only transitions likely to occur are those for which total electron spin is conserved. Thus if the final spin quantum numbers of the individual particules are s_3 and s_4, then one of the numbers, $(s_3+s_4), \ldots, |s_3-s_4|$, must be included in the set, $(s_1+s_2), \ldots, |s_1-s_2|$, which was initially possible for S.

Collisions between N^+ and the rare-gas atoms or N_2 are relatively simple since these targets have no low-lying states which might mix with the low-energy states of N^+. In the present work it was observed that the Wigner rule applied quite rigorously in these collisions.

Inelastic N^+-O_2 collisions are a more severe test of the spin-conservation rule. Since N^+ and O_2 each possess two unpaired orbital electrons in their ground states, both species have several low-lying excited states. These states as well as the ground states of N^+ and O_2 must correlate to produce a large number of low-lying states in the N^+-O_2 collision complex. The crossings and pseudocrossings of the potential-energy surfaces associated with these states could provide for the spin-orbit coupling which would result in spin-nonconserving transitions. The present results suggest that such transitions are more probable in N^+-O_2 collisions than in the less-complex collision systems.

APPARATUS

Previous investigations of spin conservation in heavy-particle collisions have been optical experiments wherein collisionally excited species were detected by the postcollision observation of photons emitted as excited atoms or molecules relaxed to lower states.[3,4] The detection of spin-forbidden products in an optical experiment is subject to question because of the possibility of these products having resulted from some secondary process. Excitation by low-energy secondary electrons is such a process.

In the present experiments, inelastic collisions are detected by means of direct measurement of the collision inelasticity. The apparatus used in these experiments is an ion-impact energy-loss spectrometer. It has been described previously[5] and only a brief outline of its operation will be given here. A beam of ions is extracted from a duoplasmatron ion source[6] and magnetically mass analyzed. This beam is decelerated from 6 keV to about 10 eV and velocity selected by passage through a hemispherical electrostatic deflector. Ions with energies falling within the deflector's 0.17-eV bandpass are reaccelerated and injected into a collision chamber containing a static gas target. Some fraction of the scattered ions are collected by an analyzer wherein they are decelerated and velocity analyzed by a second hemispherical deflector. In operation, the second deflector is set to pass ions which have suffered no energy loss. The energy-loss spectrum is scanned by progressively adding back energy to the scattered ions before they enter the second deflector system. A plot of the intensity of scattered ions, as a function of energy lost, is a spectrum which is analagous in many respects to an optical-absorption spectrum. A change in the internal energy of either the projectile ion or the target molecule is reflected by a complimentary change in the kinetic energy of the projectile. Thus a change in internal energy appears as a feature in the energy-loss spectrum.

In all of these experiments the projectile has been N^+. This ion is unusual in that the ground state is a triplet—^3P. The ion has low-lying singlet states 1.90 eV (^1D) and 4.05 eV (^1S) above the ground state.[7] These two states are metastable. The forbidden optical transitions between these states and the ground state constitute the N II *nebulium* lines.[8]

The target atoms and molecules have included He, Ne, Ar, N_2, and O_2. With the exception of O_2, all of these have singlet ground states. The oxygen molecule, like N^+, has nonzero electron-spin angular momentum when it is in its ground state. O_2 has a $^3\Sigma_g^-$ ground state. Similar to N^+, the molecule has low-lying singlet states 0.98 eV ($^1\Delta_g$) and 1.63 eV ($^1\Sigma_g^+$) above the ground state. The forbidden optical transitions between these singlet states and the triplet ground state constitute the *infrared-atmospheric* and *atmospheric*-oxygen bands.[9]

RESULTS

The energy-loss spectrum of 3.5-keV N^+ scattered from He, which is shown in Fig. 1(b), is typical of all of the observed spectra of N^+ scattered from targets which are in singlet states.[10] The prominent features at 2.15 and -2.15 eV involve metastables in the ion beam. The 2.15-eV peak corresponds to the $^1S \leftarrow {}^1D$ transition in the N^+ (^1D) ions in the beam. The feature at -2.15 eV is the result of superelastic scattering of the ^1S component of the beam via the $^1S \rightarrow {}^1D$ transition.

In addition to the peaks at ± 2.15 eV, there are very-weak peaks at ± 1.90 eV which correspond to the $^1D \leftarrow {}^3P$ and $^1D \rightarrow {}^3P$ transitions. In collisions of N^+ with targets which are in singlet states, the $^1D \leftarrow {}^3P$ transition results from a collision for which the initial total-spin quantum number

$$S_i = s_1 + s_2 = 1$$

and the final total-spin quantum number

$$S_f = s_3 + s_4 = 0 .$$

Thus the $^1D \leftarrow {}^3P$ transition, and likewise the $^1D \rightarrow {}^3P$ transition, are spin nonconservative.

As shown in Fig. 1(a), the spectrum of N^+ scattered from O_2 is quite different from those of N^+ scattered from singlet-state targets. Included in the O_2 spectrum are both inelastic and superelastic events involving transitions in ground-state N^+, metastable N^+, and the O_2 target, as well as simultaneous transitions in both projectile and target. The various identifiable features are labeled. Of all the transitions observed in this spectrum only the peak at 3.13 eV—$N^+(^1D) + O_2(X^3\Sigma_g^-) \rightarrow N^+(^1S) + O_2(^1\Delta_g)$—is the result of a spin-nonconservative process. For this process the total-spin angular momentum changes from 1 to 0. The angular profiles of several features in the O_2 spectrum have been determined by rotating the scattered-ion analyzer about the center of the collision chamber. These results are presented in Fig. 2.

DISCUSSION

Composition of the Beam and Cross Sections

As indicated in Fig. 2, the inelastic and superelastic scattering processes reported here result in angular profiles of scattered ions which are

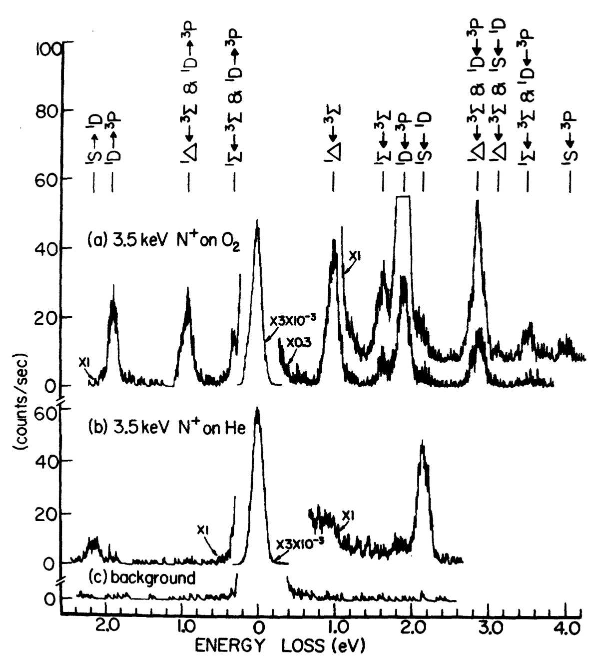

FIG. 1. (a) Energy-loss spectrum of 3.5-keV N^+ scattered from O_2. The scattering angle was 0° and the target gas pressure was 5.5 mtorr. (b) Energy-loss spectrum of 3.5-keV N^+ scattered from helium at 0° and 6.0 mtorr. (c) Energy spectrum of primary beam taken at 0° and with no gas in the collision chamber. All spectra were taken with a count-rate meter at a scan speed of 1.0 eV/min.

strongly peaked in the forward direction. A modification of the energy-loss spectrometer for measuring total cross sections for this sort of phenomena has been described previously.[11] In this device the total intensity of a transition is determined by collecting all of the scattered ions which have suffered an energy change within about 0.3 eV of the transition energy. With the modified apparatus it has been possible to determine the total cross section for the $^1S \leftarrow {}^1D$ and the $^1S \rightarrow {}^1D$ transitions in collisions of N^+ with the singlet-ground-state targets (ignoring the small intensity contributions from the spin-nonconservative transitions).[12]

Unfortunately the total-cross-section device has a relatively large entrance aperture and cannot provide the energy resolution required to separate the peaks in the O_2 spectrum. Crude cross sections can be obtained from the data in Fig. 2 by integrating over the angular profile of each peak. By this method the cross section is

$$\sigma = \frac{\int I \sin\theta\, d\theta}{\int I_0 \sin\theta\, d\theta} \frac{1}{nl}, \tag{1}$$

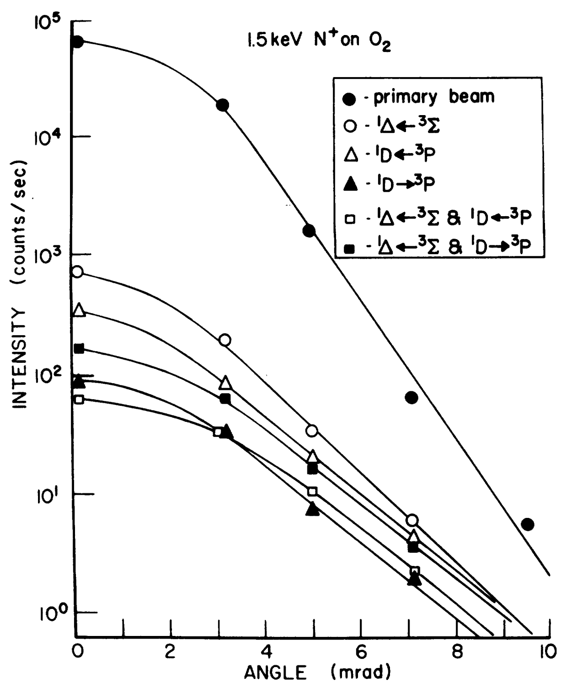

FIG. 2. Signal intensity as a function of angle as ion analyzer was rotated about the center of the collision chamber. A 1.5-keV-N^+ beam was incident on O_2 at 6.0 mtorr. The angular profile of the primary beam is shown along with the profiles of inelastically scattered ions which have lost 0.98 eV (open circles), 1.90 eV (open triangles), and 2.88 eV (open squares) and superelastically scattered ions which have gained 0.92 eV (solid squares) and 1.90 eV (solid triangles).

where I is the intensity of a spectral peak; I_0 is the intensity of that fraction of the primary beam which is in the initial state of the transition being considered; n is the number density of scatterers; and l is the length of the collision chamber. Such cross sections may be regarded as lower limits to the true values since Eq. (1) tends to overestimate the scattering volume by ignoring large-angle scattering which occurs near the entrance and exit of the collision chamber. As will be shown below, it is possible to use the available data to estimate the metastable population of the primary beam.

Clearly there is a significant metastable component in the N^+ beam which is extracted from a duoplasmatron ion source. In inelastic collisions of the beam ions, the relative intensity of each transition is a function of the beam population and the cross section for that transition. In the spectra of N^+ scattered from singlet targets, the ratio of the total intensities of the peaks at ± 2.15 eV is

$$\frac{I(^1S \rightarrow {}^1D)}{I(^1S \leftarrow {}^1D)} = \frac{\sigma(^1S \rightarrow {}^1D)}{\sigma(^1S \leftarrow {}^1D)} \frac{N(^1S)}{N(^1D)}, \tag{2}$$

where $N(^1S)$ and $N(^1D)$ are the populations in the primary beam of the indicated states and the σ's are cross sections for the indicated processes. Assuming a Boltzmann distribution of states in the beam, Eq. (2) becomes

$$\frac{I(^1S \rightarrow {}^1D)}{I(^1S \leftarrow {}^1D)} = \frac{\sigma(^1S \rightarrow {}^1D)}{\sigma(^1S \leftarrow {}^1D)} \frac{g(^1S)\, e^{-E_S/kT}}{g(^1D)\, e^{-E_D/kT}}, \tag{3}$$

where the statistical weights $g(^1S) = 1$ and $g(^1D) = 5$, and E_S and E_D are the energies of the ^1S and ^1D states. By the principle of microscopic reversibility, the ratio of cross sections in Eq. (3) is simply the ratio of the statistical weights of the

TABLE I. Typical cross sections for processes observed in the energy-loss spectra of 1.5-keV N^+ scattered from O_2 and He, Ne, Ar, and N_2. The O_2 cross sections are based upon Eq. (1). All cross sections assume the beam composition derived in the text.

Transition [a]	Energy loss (eV)	Cross section (cm^2 at 1.5 keV)
$N^+(^3P) + O_2(X^3\Sigma_g^-) \rightarrow N^+(^3P) + O_2(a^1\Delta_g)$	0.98	1.6×10^{-17}
$N^+(^3P) + O_2(X^3\Sigma_g^-) \rightarrow N^+(^1D) + O_2(X^3\Sigma_g^-)$	1.90	6.3×10^{-18}
$N^+(^3P) + O_2(X^3\Sigma_g^-) \rightarrow N^+(^1D) + O_2(a^1\Delta_g)$	2.88	2.6×10^{-18}
$N^+(^1D) + O_2(X^3\Sigma_g^-) \rightarrow N^+(^3P) + O_2(X^2\Sigma_g^-)$	−1.90	1.3×10^{-17}
$N^+(^1D) + O_2(X^3\Sigma_g^-) \rightarrow N^+(^3P) + O_2(a^1\Delta_g)$	−0.92	3.1×10^{-17}
$N^+(^1D)$ + He, Ne, Ar, or O_2 $\rightarrow N^+(^1S)$	2.15	7.4×10^{-18}

[a] Term assignments and energies from Refs. 7 and 9.

final states of the transitions

$$\frac{\sigma(^1S\rightarrow{}^1D)}{\sigma(^1S\leftarrow{}^1D)}=\frac{g(^1D)}{g(^1S)}=5\,.$$

Substituting in Eq. (3) gives

$$\frac{I(^1S\rightarrow{}^1D)}{I(^1S\leftarrow{}^1D)}=e^{-(E_S-E_D)/kT}\,. \tag{4}$$

From total intensity measurements this ratio has been determined to be

$$\frac{I(^1S\rightarrow{}^1D)}{I(^1S\leftarrow{}^1D)}=0.20\pm0.04\,.$$

Using Eq. (4), this intensity ratio gives a temperature, $T=15\,600\pm2000\,^\circ\mathrm{K}$. The population ratio corresponding to this temperature is

$$N(^1S):N(^1D):N(^3P)=1:25:182.$$

This population ratio along with the data in Fig. 2 has been used to estimate cross sections for some of the transitions observed in collisions of 1.5-keV N^+ with O_2. These results are given in Table I. The value of $\sigma(^1S\leftarrow{}^1D)$ for collisions of 1.5-keV N^+ with singlet-state targets has been calculated assuming a Boltzmann distribution among N^+ states in the beam.[12] This result is also in Table I.

An equation analagous to Eq. (4) can be derived for the N^+-O_2 collisions:

$$\frac{I(^1D\rightarrow{}^3P)}{I(^1D\leftarrow{}^3P)}=e^{-(E_D-E_P)/kT}\,.$$

This ratio has been estimated by integrating the appropriate data from Fig. 2 with respect to $\sin\theta d\theta$ [as in Eq. (1)]. The temperature determined by this means, 17 400 °K, is in agreement with the more precise value given above.

The small angular deflections which characterize the processes reported herein, as well as the large cross sections, indicate that these processes occur at large impact parameters. In terms of the adiabatic criterion of Massey,[13] the large cross sections are not surprising because of the small energy defects involved. For example, the adiabatic criterion predicts that the maximum cross section for a 1-eV process in an N^+-O_2 collision, with an interaction distance of 7 Å, occurs at a collision energy of 2.1 keV.

Wigner Rule

In the spectra of N^+ scattered from He, Ne, Ar, and N_2, the ratio of intensities of the transitions originating in the ^1D state—$^1D\rightarrow{}^3P$ and $^1S\leftarrow{}^1D$—is about 0.02. This is in spite of the fact that the ratio of statistical weights of the final states favors the less-intense transition $[g(^3P)/g(^1S)=9]$. Furthermore, if both transitions were spin conservative, it would not be unreasonable to assume that the cross sections for these two processes would be about equal since the energy defects involved are about equal. Thus the ratio of intensities of these two transitions suggests that the probability of a spin-nonconservative transition is only about 0.002 that of a spin-conservative transition.

In the spectrum of N^+ scattered from O_2, the "forbidden" peak at 3.13 eV $[N^+(^1D)+O_2(X\,^3\Sigma_g^-)\rightarrow N^+(^1S)+O_2(a^1\Delta_g)]$ is a weak, but persistent, feature, although the intensity of this peak was only reproducible to within a factor of 2. The intensity of this peak is nearly two orders of magnitude less than that of the transition at -0.92 eV $[N^+(^1D)+O_2(X^3\Sigma_g^-)\rightarrow N^+(^3P)+O_2(a^1\Delta_g)]$ which originates in the same initial state of N^+. In this case, however, the ratio of statistical weights of the final states of N^+ favors the more-intense transition $[g(^1S)/g(^3P)=\frac{1}{9}]$. This suggests that in the N^+-O_2 collision there is only a difference of about one order of magnitude between the spin-nonconservative and spin-conservative transition probabilities.

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[12] These cross sections as reported in Ref. 10 are in error by a factor of 0.48.

[13] Reference 2, pp. 441–450.