Angular distributions of N^+ from N_2^{2+} produced by electron impact on N_2

Hyuck Cho
Department of Physics, Chungnam National University, Daejeon 305-764, Korea
and Center for Molecular Sciences, Daejeon 305-701, Korea

Sang-Eon Park
Department of Physics, Chungnam National University, Daejeon 305-764, Korea

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Coincidence measurements of the angular distributions of N^+ dissociated from N_2^{2+} produced by electron impact on N_2 have been made. With an incident electron energy of 60 eV, 3.9-, 5.0-, and 7.2-eV N^+ ions were detected separately using the time-of-flight and coincidence method at selected angles between 40° and 140°. The results show flat angular distributions and the flatness for each case could be ascribed to different origins.

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I. INTRODUCTION

Angular distributions of molecular dissociation products have been of interest since Dunn [1] reported a selection rule based on symmetry. Measurements have been made mostly for H_2, N_2, and O_2, and the results at the threshold have shown good agreement with the selection rule [2–11]. However, in most experiments, only singly ionized dissociation products from one of the following processes, taking N_2 as an example, were detected without coincidence requirement:

$$e+N_2 \rightarrow N_2^+ +2e \rightarrow N^+ + N+2e \ , \quad (1)$$

$$e+N_2 \rightarrow N_2^{2+} +3e \rightarrow 2N^+ +3e \ . \quad (2)$$

A few experiments [9,11,12] have detected doubly ionized dissociation products and have determined their angular distributions. Although some experiments [13–15] have employed coincidence detection to measure the energy distributions of singly ionized products dissociated from doubly ionized parent molecules, no experiment done so far has measured the angular distribution with a coincident energy-selection mechanism. Therefore, to the authors' knowledge, the angular distribution of singly ionized dissociation products from doubly ionized parent molecules has not yet been reported.

Even in the experiments [13–15] where the energy distributions of singly ionized products dissociated from doubly ionized molecules were measured, attempts to assign the sources of these singly ionized products showed discrepancies. By measuring the angular distributions of singly ionized dissociation products and by applying Dunn's selection rules to the resultant distributions, we can have information on symmetries of the electronic states of doubly ionized molecules involved in the production of the dissociation products. This information on symmetries is important in assigning the electronic states of doubly ionized parent molecules from which the singly ionized molecules we observe come.

In this experiment, measurements of the angular distributions of N^+ ions dissociated from N_2^{2+} produced by electron impact on N_2 have been made employing time-of-flight (TOF) and coincidence techniques. Energy-selected N^+ ions, 3.9, 5.0, and 7.2 eV, were detected in coincidence for angles between 40° and 140°. The results showed flat angular distributions and the flatness for each case can be ascribed to different origins, which will be discussed in detail in the following sections.

II. BACKGROUND

Before describing the details of the present experiment, it might be useful to review the experimental attempts made so far to measure the angular distributions of dissociation products. The description will focus on N_2. When a molecule is dissociated by electron impact, the angular distribution of the dissociation products is generally anisotropic, and Dunn [1] has shown that the distribution depends on the symmetry of the initial and final molecular electronic states. Based on his argument, Dunn has derived selection rules for the transitions between pairs of electronic states for homonuclear and heteronuclear diatomic molecules. Experimental determinations of the angular distributions of H^+ from

$$e+H_2 \rightarrow H^+ + H+2e \quad (3)$$

have been reported by Dunn and Kieffer [2], Van Brunt and Kieffer [3], Kieffer and Dunn [4], Köllman [5], Crowe and McConkey [7], and others, and these results have shown good agreement, at least qualitatively, with Dunn's selection rules near threshold. The angular distributions of singly ionized dissociation fragments from N_2 and O_2 have also been measured, without using coincidence detection, by several groups—for example, Van Brunt and Kieffer [16].

To detect singly ionized dissociation fragments from doubly ionized parent molecules, coincidence detection must be used. Stockdale [13] and Edwards and Wood [15] employed this coincidence requirement in measuring the energy distributions of N^+ from N_2^{2+}. So far, to the authors' knowledge, no experiment has employed coincidence detection to measure the angular distributions of dissociation fragments from any doubly ionized molecules. This is probably due to difficulties from the very low counting rates. The angular distributions of N^{2+} from N_2^{2+}, which can be detected without coincidence

TABLE I. Calculated potential energies and equilibrium internuclear distances of the electronic states N_2^{2+}.

	Taylor[a]		Wetmore and Boyd[b]		Olsson, Kindvall, and Larsson[c]		Cobb, Moran, and Borkman[d]		Hurley[e]		Senekowitsch *et al.*[f]	
Terms	T_e (eV)[g]	r_e (Å)	U_e (eV)[h]	r_e (Å)	T_0 (eV)[i]	r_e (Å)	T_e (eV)[j]	r_e (Å)	T_e (eV)[j]	r_e (Å)	T_e (eV)[a]	r_e (Å)
$X\,^1\Sigma_g^+$	0	1.139	42.8	1.16	0	1.138	41.7	1.259	42.77	1.15		
$^1\Pi_u$	2.3	1.266	44.1	1.28			42.36	1.19	43.43	1.24		
$^1\Sigma_u^+$	9.1	1.140			8.09	1.144						
$^3\Pi_u$	0.6	1.254	42.7	1.25			41.97	1.18	42.15	1.22		
$^3\Sigma_g^-$	1.5	1.379					41.10	1.26	42.57	1.31		
$^3\Sigma_u^+$	1.5	1.109	44.5	1.12							1.57	1.094
$^1\Delta_g$			44.2	1.40								
$^3\Pi_g$			46.4	1.23							3.54	1.201

[a]Reference [24].
[b]Reference [25].
[c]Reference [30].
[d]Reference [23].
[e]Quoted from Ref. [23], original from Ref. [21].
[f]Reference [26].
[g]Potential minima of $X\,^1\Sigma_g^+$ are 42.8 eV above $v=0$ of $X\,^1\Sigma_g^+$ of N_2, and 4.0 eV above $N^+(^3P)+N^+(^3P)$.
[h]Potential energy is relative to $v=0$ of $X\,^1\Sigma_g^+$ of N_2.
[i]$v=0$ of N_2^{2+} $X\,^1\Sigma_g^+$ is 42.1 eV above $v=0$ of N_2 $X\,^1\Sigma_g^+$.
[j]Relative to the equilibrium energy of N_2, using the basis set two (see Ref. [23]).

techniques, have been reported by Deleanu and Stockdale [12] and Crowe and McConkey [9,11]. None of the above results, where near-threshold data are available, has shown a significant contradiction with Dunn's selection rules.

Even though the experimental and theoretical data on doubly ionized molecules are essential for the study of the angular distributions of dissociation fragments, only a limited amount of data is available. In the case of a nitrogen molecule, in addition to the experimental works mentioned above, Krishnakumar and Srivastava [17] measured the branching ratio of the ions from nitrogen molecules, Cosby, Moller, and Helm [18] did photofragment spectroscopy of N_2^{2+}, and Curtis and Boyd [19] worked on the predissociations of several doubly ionized molecules including the nitrogen molecule. On the theoretical side, the situation is not better. There has even been disagreement on the ground state of N_2^{2+} until recently [20]. The potential curves of this doubly ionized molecule have been calculated by some researchers. Hurley [21] reported his semiempirical calculations, and Thulstrup and Andersen [22] used *ab initio* calculations. In the work of Cobb, Moram, and Borkman [23], a self-consistent-field (SCF) method was used. Later, Taylor [24], Wetmore and Boyd [25], Taylor and Partridge [20], and Senekowitsch *et al.* [26] presented the calculations using various techniques. Some information from these results is summarized in Table I; the data in Table I are not directly comparable because they were tabulated without normalization, partly due to some missing parameters in the original papers.

III. EXPERIMENTS AND RESULTS

The experimental setup used in this experiment was basically the same as the one used in previous experiments [27–29], but with the capability of angular detection added. A schematic diagram of the scattering region is shown in Fig. 1. An electron beam generated from a hot tungsten filament was passed through a gate with a pair of deflecting plates inside to make a pulsed beam. The full width at half maximum (FWHM) of the gun pulse width was reduced to about 15 ns compared to that of the previous experiments. The energy of the electrons incident on the target was adjusted to 60 eV, and the currents of the dc and pulsed electron beams were maintained at a little less than 1 μA and a few nA, respectively. The reason for choosing just one, 60-eV incident energy will be given in Sec. IV. The molecular nitrogen target gas was introduced into the scattering region through a stainless steel tube with an inside diameter of about 2 mm. The pressures inside the vacuum chamber before and after the introduction of the gas were about 8×10^{-7}

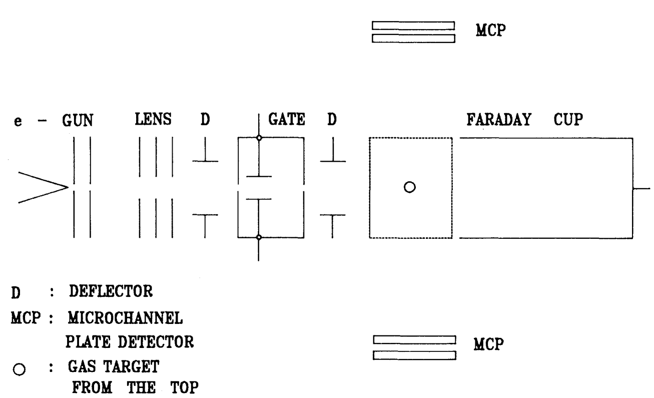

FIG. 1. Schematic diagram of the core part of the experiment.

and 1×10^{-5} Torr, respectively, when measured away from the scattering region with an ionization gauge. The effects of the long-term variations of the electron current and the target gas pressure were normalized by frequently measuring the signals at 90° with respect to the incident electron-beam direction during the course of the experiments.

Two N^+ ions dissociated from N_2^{2+} were directed in opposite directions upon each double ionization by electron collision with the target. Ions having directions between 40° and 140° with respect to the electron-beam axis were detected by a pair of microchannel plate detectors which were located 20 cm away from the center of the scattering region as shown in Fig. 1. The signals measured at an angle θ were multiplied by $\sin\theta$ to correct for changes in the interaction volume as the angle changed. The Faraday cup was removable to give a path to the detectors, and the range of the detector angle was limited by the geometry of the system.

To measure the kinetic-energy distribution of N^+ ions dissociated only by double ionizations, a standard TOF technique was employed with a cation-cation coincidence requirement. The circuit logic for the TOF measurement with the coincidence requirement in Ref. [27] was used with some modifications. In the detection circuit, two detector signals were fed into a universal coincidence unit after discrimination and amplification. In this experiment, the angular distributions of ions with a preset energy, instead of the entire energy range, were measured at detector angles between 40° and 140° in 10° steps. To discriminate N^+ ion signals of a preset energy from the energy spectrum, a gate was used in one detector channel. The preset N^+ energies were 3.9, 5.0, and 7.2 eV. At each of these energies, N^+ signals from this channel in coincidence with signals from another, ungated channel were fed into a universal coincidence unit followed by a counter. The reason for choosing the above energies will be discussed in the next section. The number of angle points was limited by the extremely low counting rates.

Possible major sources of uncertainty in the determination of the kinetic energy are (1) the uncertainty due to the finite electron-beam pulse width of 15 ns, (2) the uncertainty in the determination of the flight-path length due to the finite size of the electron beam, and (3) the uncertainty in the measurement of the flight-path length. A generous estimate of the total uncertainty in the kinetic energy varies from 0.1 to 0.2 eV, depending on the time of flight. The background subtraction was accomplished by measuring the ungated signals as done in the previous experiment [27]. The angular distributions of the 3.9-, 5.0-, and 7.2-eV N^+ ions dissociated from N_2^{2+} produced by electron impact on N_2 are given in Fig. 2.

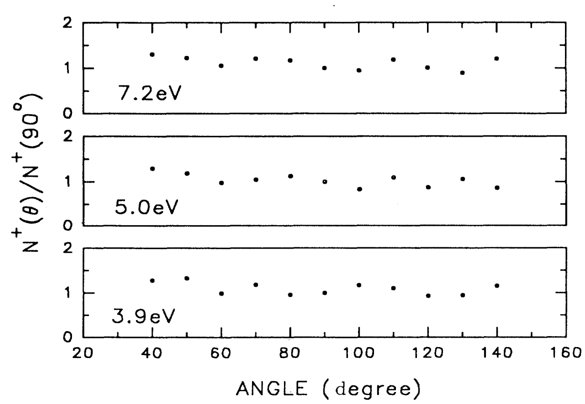

FIG. 2. Angular distributions of N^+ ions dissociated from N_2^{2+} produced by electron impact on N_2.

IV. DISCUSSION

Since Dunn's selection rules apply near the threshold region, the electron-impact energy in this experiment has to be near the threshold region for double ionization of nitrogen molecules. The experimental and theoretical studies done so far suggest that the potential energies of the doubly ionized N_2 state in the Franck-Condon region lie mostly between 40 and 50 eV. Therefore the electron-impact energy should not be much greater than 50 eV. In this experiment, an electron energy of 60 eV was chosen [2].

As mentioned already, one angular distribution measurement must be made at one selected, preset kinetic energy of the ion, and the next measurement at the next kinetic energy. To choose these preset energies, energy distributions of the N^+ ion measured in coincidence must be referenced. In the electron-impact result of Stockdale [13], the total-kinetic-energy release peaks appeared near 6 and 8 eV. Another electron-impact result obtained by Brehm and DeFrênes [14] showed the peaks near 7, 9.7, and 14 eV; a similar result was obtained by Edwards and Wood [15] whose peaks were placed near 7.8, 10.2, and 14.8 eV. The kinetic energy of N^+ from N_2^{2+} is half of the above total-kinetic-energy release. Combining these results with other experimental [12,19] and theoretical results, the three energies of N^+ dissociated from N_2^{2+} at which the angular distribution measurements were to be made were chosen: 3.9, 5.0, and 7.2 eV. These energies may not happen to be at the maxima of the peaks contributing to the respective energy distributions; however, counting the finite width of the Franck-Condon region, they are believed to be at least on the shoulders of the peaks, which can at worst result in an increased data-collection time. If a larger number of preset energies had been chosen, this study would have been more thorough. However, the extremely low counting rate and the resulting long data-collection time, which was typically more than a week at each data point, made more measurements impossible.

All the angular distributions at these energies (see Fig. 2) show almost flat isotropic features except possible indications of the rising of small peaks to the forward direction. The forward anisotropies have been observed in other results [11], where they have been explained as a result of momentum transferred to N_2 by the incident electrons.

The angular distribution of the 7.2-eV ions is isotropic and took the longest data-collection time. It has been believed that the $^1\Sigma_u^-$ state is a very strong candidate for a contributor to this ion energy [15,19]. According to

Dunn's selection rules, a transition from $^1\Sigma_g^+$ to $^1\Sigma_u^-$ is forbidden in both the perpendicular and parallel directions with respect to the incident electron-beam axis. This forbidden transition may explain the isotropy and the even lower counting rate. The forbiddenness does not mean that there will be absolutely no counting rate in any direction for an incident electron energy of 60 eV.

Contrary to the angular distribution of 7.2-eV ions, the interpretations of the 5.0- and 3.9-eV data must be different even though they have also produced isotropic distributions. Near the electronic state(s) which might contribute to the 5.0- and 3.9-eV ions, many closely spaced states are believed to exist. Counting the closeness of these states—sometimes, less than a few tenths of 1 eV—and the broad width of the Franck-Condon region of N_2^{2+} in terms of energy, around 1 eV [25], the TOF technique has natural limits and can hardly resolve these states. Therefore it can be concluded that the flatness of the angular distributions of the 5.0- and 3.9-eV ions may be due to contributions from several electronic states having different symmetries. Edwards and Wood observed the coincidence peaks at 7.4, 5.1, and 3.9 eV. They also predicted that the $^1\Pi_u$ state would produce the 4.1-eV ions and the $^3\Sigma_g^-$, $^3\Pi_g$, and $^1\Delta_g$ states the 4.7–5.0-eV ions. Curtis and Boyd obtained similar results. The transitions from the $^1\Sigma_g^+$ state to the $^3\Sigma_g^-$ and $^3\Pi_g$ states are forbidden in both the perpendicular and parallel directions and a transition to the $^1\Delta_g$ state is allowed in perpendicular direction. Therefore, if only these three states were contributing to the production of ions near 5 eV, it would seem probable that the angular distribution of the 5.1-eV ions would have a higher counting rate around 90°. However, there is no indication of this anisotropy in the angular distribution, and this might suggest that one or more states other than these three states may also be contributing to the 5-eV ions.

V. CONCLUSIONS

In this experiment, measurements of the angular distributions of N^+ dissociated from N_2^{2+} produced by electron impact on N_2 have been made employing time-of-flight and coincidence techniques. Energy-selected N^+ ions, 3.9, 5.0, and 7.2 eV, were detected in coincidence for angles between 40° and 140°. All the angular distributions at these energies show almost flat isotropic features except for possible indications of little anisotropies in the forward direction. The angular distribution of the 7.2-eV ions is isotropic and took a longer data-collection time than average. It has been believed that the $^1\Sigma_u^-$ state is a very strong candidate as a possible contributor to this ion energy. The forbidden transition to the $^1\Sigma_u^-$ state according to Dunn's selection rules and the low counting rate may support this interpretation. Contrary to the angular distribution of the 7.2-eV ions, the interpretations of the 5.0- and 3.9-eV data must be different even though they also produced isotropic distributions. Counting the closeness of the states contributing to the ions with these energies and the broad width of the Franck-Condon region of N_2^{2+}, it can be concluded that the flatness of the angular distributions of the 5.0- and 3.9-eV ions might be due to contributions from several electronic states having different symmetries. In addition, evidence exists which suggests that one or more states other than the $^3\Sigma_g^-$, $^3\Pi_g$, and $^1\Delta_g$ states may also contribute to the 5-eV ions.

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