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**FAST TRACK COMMUNICATION**

# Direct evidence for channel-coupling effects in molecules: electron impact excitation of the $a'' \, ^1\Sigma_g^+$ state of $N_2$

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**Abstract**

New measurements of differential cross-sections for excitation of the $a'' \, ^1\Sigma_g^+$ ($v' = 0, 1$) state in molecular nitrogen reveal a cusp-like angular distribution. This feature is distinctly observed for the first time in the present electron energy-loss experiment as a result of finer scattering angle grid and impact energy coverage than previous measurements. This feature is similar to that observed in atomic targets such as He, Hg and Ba. The observed phenomenon suggests an interference effect related to configuration–interaction coupling between lower and excited states that are of the same symmetry. It is hoped that the present work will stimulate theoretical investigations into the physics that governs this cusp-like behaviour.

(Some figures in this article are in colour only in the electronic version)

Electron impact excitation of atomic and molecular targets is of continuing importance in our understanding of a host of natural and man-made phenomena, including aurora [1], airglow [2], plasma sterilization [3] and lighting technologies [4, 5]. Considerable effort has been made in the past to both theoretically and experimentally determine electron scattering cross-sections for these targets. Whereas significant progress has been made for atomic targets [5–7], particularly through benchmarking against distinguishing experimental features such as resonances [8, 9] and electron impact coherence parameters [10, 11], even homonuclear diatomic molecular targets (e.g., $N_2$) remain a significant challenge to theory. This difficulty is largely on account of their reduced symmetry and additional rotational and vibrational degrees of freedom in nuclear motion, which couple into the electronic motion. Distinct molecular features observed experimentally are necessary to test and refine different theoretical approaches to better understand and quantify electron interference effects. Moreover, both

  

modelling and interpretation of optical observations of plasmas require accurate knowledge of important parameters (e.g., cross-sections, predissociation yields, etc) for the relevant processes.

In this communication, we report on an interesting channel-coupling effect observed via electron energy-loss spectroscopy for excitation of the $a''\ ^1\Sigma_g^+$ ($v' = 0, 1$) state in molecular nitrogen. To our knowledge, this feature has not previously been distinctly or directly observed. It will provide an exciting opportunity to assess different physical mechanisms contained in theoretical models for electron interference effects via electron scattering from molecules. Furthermore, the present results suggest a decrease of the $a''\ ^1\Sigma_g^+$ ($v' = 0, 1$) integral cross-section (ICS), for values derived from insufficiently resolved angular distribution measurements (i.e., differential cross-sections), which corresponds to the weak Dressler–Lutz emission at approximately 101.05 nm [12]. More importantly, the present results suggest that ICSs corresponding to important emissions (e.g., Vegard–Kaplan, Lyman–Birge–Hopfield, etc) that were normalized to the $a''\ ^1\Sigma_g^+$ cross-section (i.e., isolated energy-loss feature) are also overestimated. This assertion is further substantiated by recent experimental [13] and theoretical [14] investigations, which did not utilize the $a''\ ^1\Sigma_g^+$ state for normalization, that suggest smaller ICSs compared to previous data sets (see [14] for references). Molecular nitrogen is the major component of the atmospheres of the Earth, Titan and Triton, as well as in plasma processing. Consequently, any potential reductions in accepted ICSs for $N_2$ are of particular and widespread importance. For example, accurate determinations of the excitation cross-sections for processes in $N_2$ provide increased ability to quantitatively assess measurements by the Hubble Space Telescope, Far Ultraviolet Space Explorer and the Cassini Ultraviolet Imaging Spectrograph (representing a substantial scientific investment).

In a previous paper [15], we carried out careful and extensive energy-loss measurements on molecular nitrogen, in the energy-loss range of 6.25 eV to 11.25 eV, which covered the $A\ ^3\Sigma_u^+$ $B\ ^3\Pi_g$, $W\ ^3\Delta_u$, $B'\ ^3\Sigma_u^-$, $a'\ ^1\Sigma_u^-$, $a\ ^1\Pi_g$, $w\ ^1\Delta_u$ and $C\ ^3\Pi_u$ states and determined differential cross-sections (DCS) for excitation of these electronic levels from the ground $X\ ^1\Sigma_g^+$ ($v'' = 0$) state. Recently, we extended these measurements for excitation features in the energy-loss range of approximately 12 eV to 13.8 eV, which includes the dipole-forbidden $a''\ ^1\Sigma_g^+$, $F\ ^3\Pi_u$ and $G\ ^3\Pi_u$ states and dipole-allowed $b\ ^1\Pi_u$, $c\ ^1\Pi_u$, $o\ ^1\Pi_u$, $b'\ ^1\Sigma_u^+$ and $c'\ ^1\Sigma_u^+$ states. In general, the analysis of the energy-loss spectra in these extended measurements differs from [15] in that perturbative couplings between the Rydberg–valence and Rydberg–Rydberg $^1\Pi_u$ and $^1\Sigma_u^+$ states, along with more subtle spin–orbit couplings with the dipole-forbidden triplets [16], do not allow us to assume that the excitation of vibrational levels of electronic states follow Franck–Condon (FC) ratios when compared to the other vibrational levels [8]. In fact, Liu *et al* [17] unambiguously demonstrated that FC models are of little use for interpreting $N_2$ spectra in this energy region. The overall analysis of the spectral data thus followed a modified algorithm of Khakoo *et al* [15]. However, the $a''\ ^1\Sigma_g^+$ state, including $v' = 1$, which is close to the $b\ ^1\Pi_u$ (0) level, was found to not be affected by perturbative interactions in agreement with [8, 18]. Thus, the present analysis of the $a''\ ^1\Sigma_g^+$ state revealed that the ratio of the intensities of the $a''\ ^1\Sigma_g^+$ state vibrational levels remains in the FC ratio for their excitation from the ground $X\ ^1\Sigma_g^+$ ($v'' = 0$) state.

The determination of the DCSs for these transitions follows approximately the same recipe as was used in [15]. Briefly, energy-loss spectra were taken over a range of scattering angles ($\theta$) from $\approx 3^\circ$ to $130^\circ$ and over an energy-loss range of approximately 12 eV to 13.8 eV. A sample electron energy-loss spectrum is shown in figure 1. These spectra were unfolded using a well-established unfolding code (see [15]) that employed reliable energy-loss values for the $a''\ ^1\Sigma_g^+$, $b\ ^1\Pi_u$, $c\ ^1\Pi_u$, $o\ ^1\Pi_u$, $b'\ ^1\Sigma_u^+$, $c'\ ^1\Sigma_u^+$, $F\ ^3\Pi_u$ and $G\ ^3\Pi_u$ vibrational manifolds

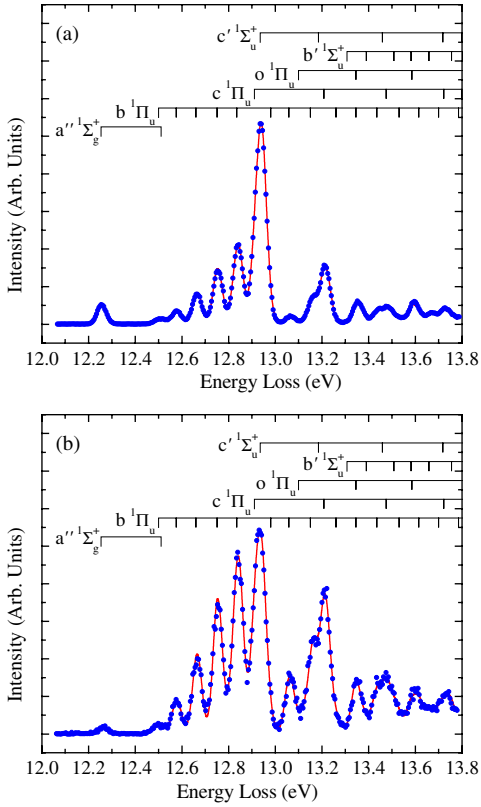


**Figure 1.** Electron energy-loss spectra of $N_2$ taken at $E_0 = 50$ eV and scattering angle of (a) 3° and (b) 20°. The positions of the various spectral lines, except the triplet valence–Rydberg states, are indicated. Note the significant relative decrease of the height of the a″ $^1\Sigma_g^+$ ($v' = 0$) state energy-loss feature (located at 12.255 eV energy loss, in (b), at the DCS minimum) as compared to (a). The dots are the present experimental data and the line is a spectral fit using energy-loss data from [18, 19].

[18, 19]. The unfolded line intensities were normalized to $N_2$ elastic electron scattering DCSs (see [15] for references) using time-of-flight experimental data for a reliable transmission correction of the spectrometer. Our DCS results will be reported in full in a longer paper [20].

The DCSs for excitation of the a″ $^1\Sigma_g^+$ ($v' = 0$, 1) state were obtained with electrons of incident energy ($E_0$) between 17.5 eV and 100 eV. It should be noted here that the a″ $^1\Sigma_g^+$ ($v' = 0$) state energy-loss line is an isolated feature, which holds ∼85–90% of the Franck–Condon factor. The analysis of the DCS for this transition is therefore considerably simplified when compared to the other vibrational manifolds. Figures 2(a) and (b) show our present relative DCSs for excitation of the a″ $^1\Sigma_g^+$ ($v' = 0$, 1) state compared to other measurements, normalized to our 60° DCS point in order to illustrate the cusp structure. Figure 2(c) shows our absolute DCS for the a″ $^1\Sigma_g^+$ ($v' = 0$, 1) state at $E_0 = 100$ eV indicating a prominent cusp structure. The cusp feature appears uniformly between the $v' = 0$ and $v' = 1$ levels of the a″ $^1\Sigma_g^+$ state within the experimental statistics. Additionally, figure 2(d) shows the ratio of the DCSs of the a″ $^1\Sigma_g^+$ ($v' = 0$, 1) state divided by the b $^1\Pi_u$ + c $^1\Pi_u$ + c′ $^1\Sigma_u^+$ sum to facilitate comparison with the energy-loss data in [24]. The DCSs reported by Furlan *et al* [24] were

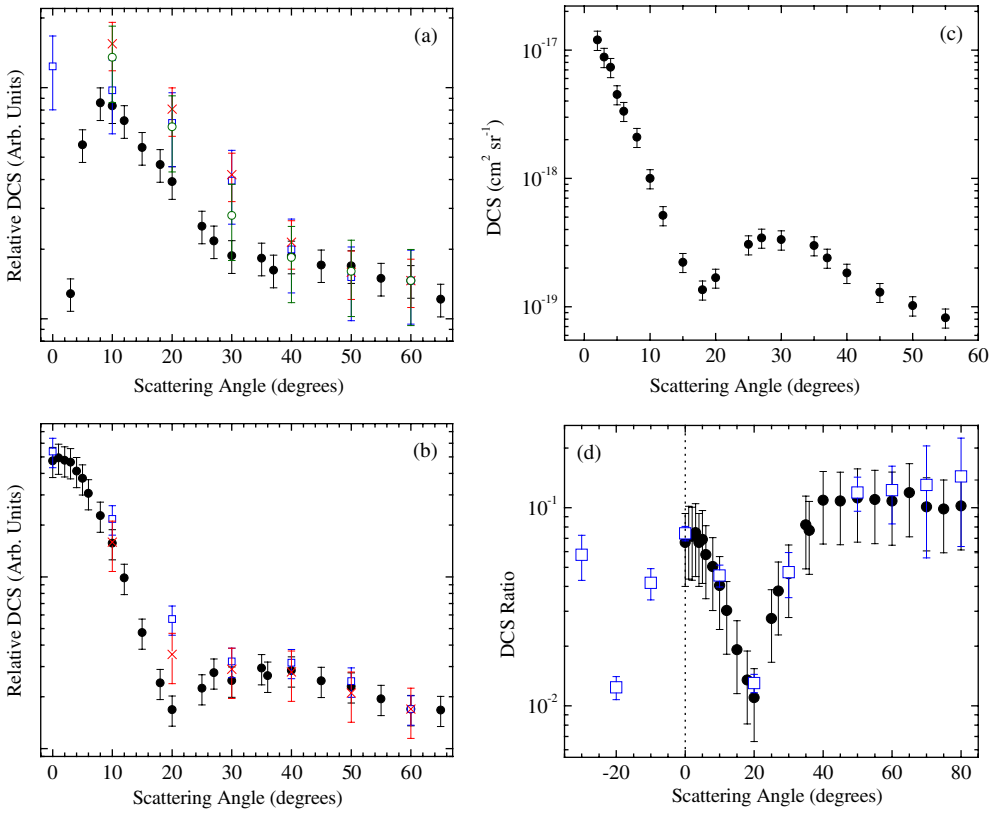


**Figure 2.** (a) and (b) Relative DCSs for the electron impact excitation of the $N_2$ a$''$ $^1\Sigma_g^+$ (v$'$ = 0, 1) state from the X $^1\Sigma_g^+$ (v$''$ = 0) ground state; $E_0$ values: (a) 17.5 eV and (b) 30 eV are shown on a relative scale alongside other data sets that have been normalized to our measurements at 60° in order to emphasize both the similarities and differences in measured angular distributions. Legend: (●) present work; (□) Trajmar *et al* [21] (at $E_0 = 17$ eV); (×) Brunger and Teubner [22]; (○) Zubek and King [23]. (c) DCS at $E_0 = 100$ eV. Legend: (●) present work. (d) Ratio of the DCSs of the a$''$ $^1\Sigma_g^+$ (v$'$ = 0, 1) state divided by the b $^1\Pi_u$ + c $^1\Pi_u$ + c$'$ $^1\Sigma_u^+$ sum. Legend: (●) present work at $E_0 = 30$ eV; (□) Furlan *et al* [24] at $E_0 = 35$ eV. This ratio's denominator is an incomplete sum over the v$'$ levels of the b, c and c$'$ states. When compared to our more extensive coverage of the b, c and c$'$ levels, the denominator sum of Furlan *et al* is approximately 0.78 ± 0.03 of ours. Hence their ratio was multiplied by this factor to make the comparison. See the text for discussion.

limited to ratios of states between −30° and 80° at $E_0 = 35$ eV, which were digitized for plotting (see [24] for further details). Furthermore, the b $^1\Pi_u$ + c $^1\Pi_u$ + c$'$ $^1\Sigma_u^+$ sum is partial over the v$'$ levels of the b, c and c$'$ states due to the finite experimental energy-loss range. When compared to our more extensive coverage of the b, c and c$'$ levels, the denominator sum of Furlan *et al* is approximately 0.78 ± 0.03 of ours. Hence their ratio was multiplied by this factor to adjust for differences in vibrational contributions and make the comparison. We note that the excellent agreement illustrated in figure 2(d) provides strong support of the present results.

Several observations can be made: at $E_0 = 17.5$ eV (figure 2(a)) there is no evidence of any present or evolving cusp around the $\theta = 20°$ region. However, at $E_0 \geqslant 20$ eV (figures 2(b) and (c)) the DCS for the a$''$ $^1\Sigma_g^+$ (v$'$ = 0, 1) state falls rapidly from the forward direction developing

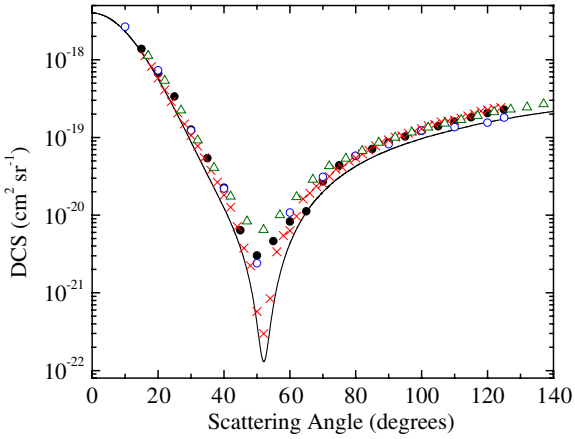


**Figure 3.** DCSs for electron impact excitation of the $2^1$S state of He from the ground $1^1$S state, at $E_0 = 40$ eV. Legend: (●) Khakoo and Larsen [25]; (○) Hall *et al* [26]; (×) Roder *et al* [27]; (△) Cubric *et al* [28]; (—) Fursa and Bray [29], convergent close-coupling method. Error bars are approximately the size of the symbols. See the text for discussion.

into a sharp cusp in the vicinity of $\theta = 20^\circ$. This minimum does not move appreciably in angular position as $E_0$ is increased. Past measurements averaged over the extent of the cusp presumably because the angular step ($\sim 10^\circ$) and possibly the angular acceptance used were too large. At incident energies of 17.5 eV and 20 eV the DCSs fall rapidly again as $\theta \rightarrow 0^\circ$, indicative of the fact that this is mainly a quadrupole-allowed transition [12] and the DCS is therefore expected to drop to zero when zero angle is approached. Furthermore, we note that interpolation between data points and a lack of sufficient angular resolution to clearly observe the cusp structure will generate an overestimation of derived ICSs of molecular nitrogen.

Whereas cusp-like behaviour has been observed in electron–atom scattering, this is the first time that it has been directly observed in electron–molecule scattering. Remarkably, for $N_2$, it is only the excitation of the X $^1\Sigma_g^+$ ($v'' = 0$) $\rightarrow$ a$''$ $^1\Sigma_g^+$ ($v' = 0, 1$) transition that displays this striking behaviour [20], i.e., when the ground and excited states have the same symmetry. We can draw an analogy of this to the $1^1$S $\rightarrow$ $2^1$S excitation in He, which is a well-studied process on both experimental and theoretical fronts (figure 3). This atomic transition also displays similar behaviour, except showing a cusp at larger angle (i.e., 50°). Importantly, for He ($n = 2$) excitation, none of the other fine-structure excitations (namely $2^3$S, $2^3$P or $2^1$P) display such behaviour, i.e., these excitations have DCSs that are not cusp-extreme, strengthening the evidence that the cusp is related to both the upper and lower states having the same symmetry. It is noteworthy that Skerbele and Lassettre [30] alluded to the symmetry connection between the He $1^1$S $\rightarrow$ $2^1$S and $N_2$ X $^1\Sigma_g^+ \rightarrow$ a$''$ $^1\Sigma_g^+$ transitions using relatively high electron impact energies over a limited angular range of approximately 2° to 6° while obtaining generalized oscillator strengths for $N_2$.

We have also looked at other electron impact excitation DCSs of atomic transitions available in the literature. Theoretical data for electron impact excitation of the $6^1$S $\rightarrow$ $7^1$S and $6^1$P $\rightarrow$ $7^1$P transitions of Ba [6] and $6^1$S $\rightarrow$ $7^1$S excitation of Hg [7, 31] also display similar behaviour. In figure 3, we note that the depth and width of the minimum depend on the angular resolution of the experiment. In the case of He, this width (at half minimum) is about 7°. The width of the minimum in $N_2$ is around 9°. However, it is not as deep. Also interesting is that discovery of these cusp-like features in inelastic scattering is easy to miss, such as is the case for the present X $^1\Sigma_g^+$ ($v'' = 0$) $\rightarrow$ a$''$ $^1\Sigma_g^+$ ($v' = 0, 1$) transition, which was

not distinctly identified by previous experimental efforts (e.g., [21–23, 32]), and for example in the $6^1S \rightarrow 7^1S$ excitation in Hg by Panajotović *et al* [33]. Again, this is because most DCS experiments sweep over scattering angle at intervals of $\sim 10^\circ$ and can thus 'jump' over such narrow phenomena.

Another interesting cusp-type DCS behaviour is associated with elastic scattering from the ($n^1S_0$) ground states of the heavy rare gases, for example the well-known very sharp cusps in the elastic scattering DCSs in Ne, which has a closed-shell structure [34].

This cusp-like behaviour suggests that some sort of the same symmetry coupling is responsible for the interference type of behaviour associated with the cusp-like minima in these DCSs. Consequently, one could suggest configuration-type channel-coupling processes propagating such behaviour, involving matrix elements between same-symmetry wavefunctions. Further, the reduced depth of the $a'' \, ^1\Sigma_g^+$ ($v' = 0, 1$) state minimum when compared to the He $2^1S$ minimum is most probably due to rotational and vibrational modes that would tend to smear out the cusp. It would therefore be very interesting from a theoretical viewpoint to investigate the role of molecular nuclear alignment and orientation by carrying out fixed-nuclei calculations.

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