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Alignment and orientation of diatomic molecules induced by polarized electron impact

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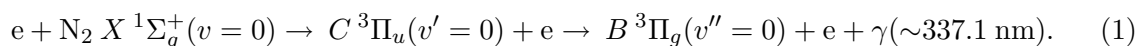
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Abstract. We report measurements of linear and circular fluorescence polarizations for molecular transitions in H₂, D₂, and N₂ induced by spin-polarized electron impact. Circular polarizations resulting from some Fulcher- α transitions in H₂ and D₂ are found to be significant, while the null results from nitrogen's second positive system are consistent with an earlier measurement by the Münster group. We compare this nitrogen data to that from our previous study of nitrogen's first negative system. Emphasis is placed on understanding the mechanisms that cause the values of circular polarization from N₂ to be relatively small compared to those observed from H₂ and D₂ molecules.

1. Introduction

Measurements of molecular fluorescence polarization resulting from spin-polarized electron impact excitation are rare compared to the number of existing studies for atomic targets. Investigation of such polarizations (Stokes parameters) has proven to be a useful means with which to probe the angular momentum coupling dynamics in excited states [1, 2]. The earliest experiment to measure the Stokes parameters for molecular fluorescence due to spin-polarized electron excitation was performed by the Münster group in Germany [3]. The integrated Stokes parameters (scattered electrons not detected) were reported for the second positive system in molecular nitrogen,



Interestingly, the observed circular polarization (spin-normalized Stokes parameter P_3/P_e) was found to be zero at ~ 14.5 eV within an uncertainty of 2×10^{-3} . This result stood in contrast with the atomic situation, where sizeable P_3/P_e values result from triplet excitation [4]. In light atoms, LS -coupling is responsible for the conversion of spin-polarization into fluorescence circular polarization. This situation is depicted schematically in Fig. 1.1. Exchange excitation of a multiplet state having $S > 0$ allows transfer of spin polarization (or orientation) from the polarized incident beam to the excited system. Then, LS -coupling of the oriented \mathbf{S} with the initially unoriented \mathbf{L} results in orientation of the total angular momentum \mathbf{J} (neglecting nuclear spin). The Stokes parameter P_3 for the subsequent spontaneous emission of the excited state is then typically non-zero when observed in a direction parallel to the incident spin polarization. Angular momentum coupling schemes for molecules are generally more complex than the LS -coupling in atoms, and vector diagrams for some selected states are illustrated in Fig. 1. Hund's

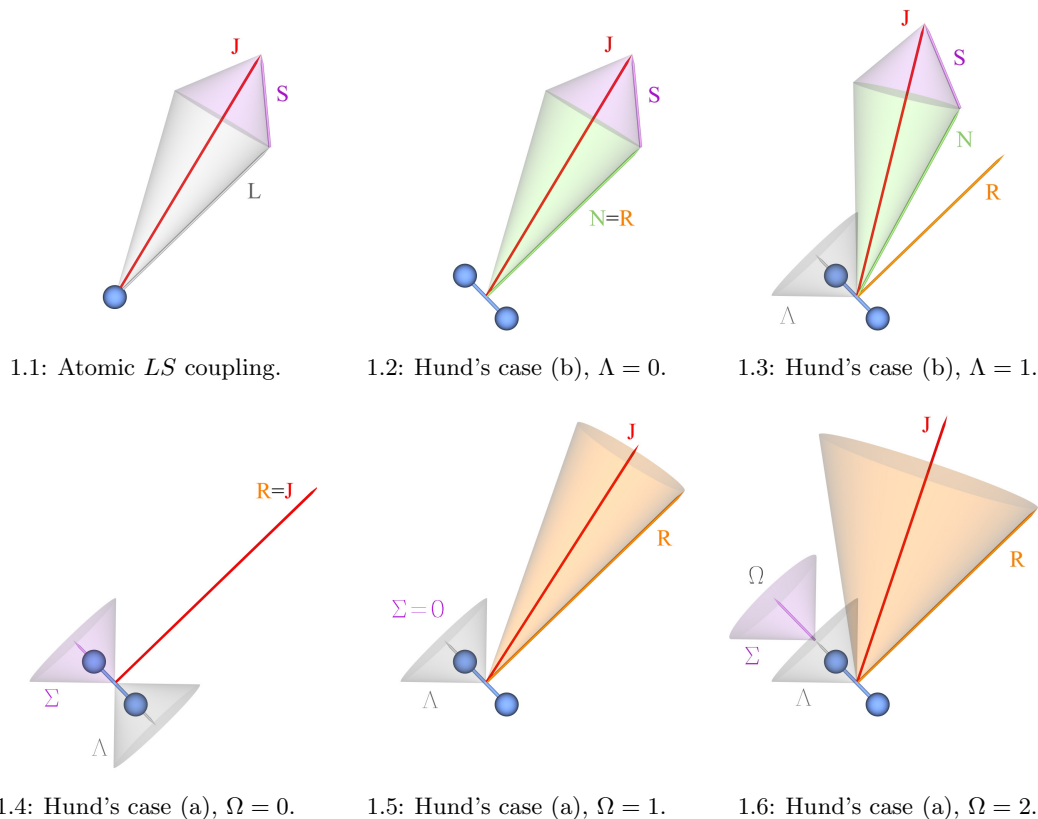


Figure 1. Angular momentum coupling in atoms and molecules. The atomic LS coupling scheme is shown in (1.1). Molecular Hund's case (b) situations for Σ ($\Lambda = 0$) and Π ($\Lambda = 1$) states are shown in (1.2) and (1.3), respectively. Hund's case (a) situations for Π states with $\Omega = 0, 1$, and 2 are shown in (1.4), (1.5), and (1.6), respectively.

cases (b) and (a) are depicted in Figs. 1.2–1.6 as they are relevant for H_2 (or D_2) and N_2 molecules, respectively. Figures 1.2, 1.3 and 1.6 indicate that orientation of S results in orientation of J . In simple analogy with the atomic case, one might expect the N_2 second positive band to exhibit non-zero values of P_3/P_e (Fig. 1.6). Thus the null values observed were a surprise.

Our group has done a number of experiments with both H_2 and N_2 targets to try understand this atomic/molecular difference. In an initial report, we presented the first measurements of non-zero circular polarization for molecular fluorescence from H_2 due to spin exchange [5]. In this paper we report recent extensions of these results to include the linear polarization (Stokes parameter P_1) and data for D_2 . We also present our verification of the Münster result for the second positive system of N_2 , and discuss mechanisms which could account for the null measurements of P_3/P_e in this case.

2. Experiment

Our experimental apparatus has been discussed in detail elsewhere [6, 7]. An unstrained Cs-O activated GaAs crystal is irradiated with 785 nm light to produce an electron beam with $\Delta E \sim 0.3$ eV FWHM and a typical transverse spin polarization of $P_e \sim 0.25$ as measured by optical polarimetry [4, 8, 9]. The beam is directed through a target gas cell; emission is collected perpendicular to the beam. A rotatable retarder followed by a polarizer and optical bandpass filter allow for determination of Stokes parameters at desired wavelengths [10].

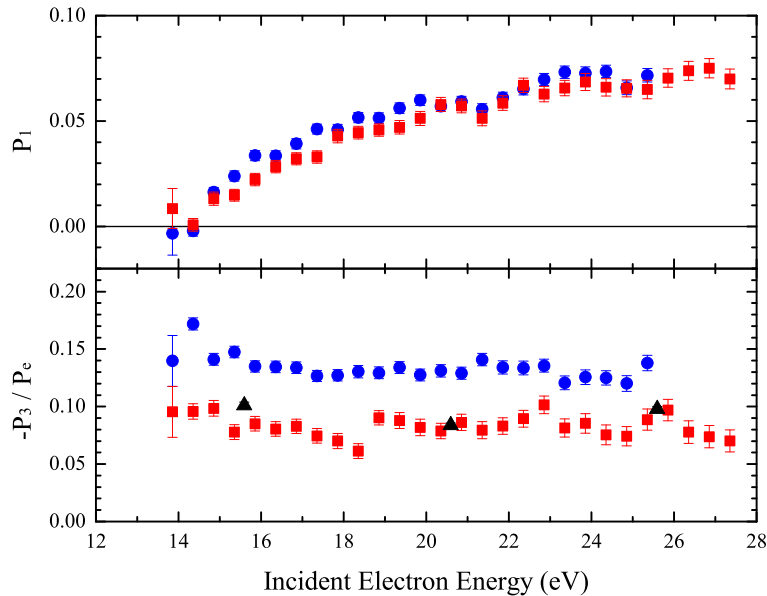


Figure 2. Linear and circular polarization fractions (P_1 and $-P_3/P_e$) for molecular transitions in H_2 (circles) and D_2 (squares). Our earlier data for H_2 is shown in triangles [5]. Data was acquired using a 600 nm (10 nm FWHM) bandpass filter; the gas pressure was 0.5 mTorr for the current results and 12 mTorr for the earlier measurements. Polarizations corresponding to the low intensities observed below 13.9 eV are omitted.

3. Linear and circular polarizations for H_2 and D_2

Our results for the linear (Stokes parameter P_1) and circular polarizations are shown in Fig. 2. The polarization P_1 is defined with respect to the electron beam and is independent of the value of P_e . The spin-normalized circular polarization is reported with a minus sign; this is done to eliminate possible confusion arising from the definition of P_3 , which has a sign opposite that of the photon helicity [2]. Positive values of $-P_3/P_e$ occur when the emitted photon angular momentum points in the same direction as the incident electron spin. The spin-normalized linear polarization P_2/P_e is not shown in Fig. 2 but is consistent with zero for both the H_2 and D_2 data sets. (The Stokes parameter P_2 is the linear polarization with respect to an axis offset by 45° from the electron beam direction.)

Due to the relatively wide bandpass of the optical interference filter used for this experiment (600 ± 5 nm FWHM), several different ro-vibrational transitions contribute to the measured Stokes parameters [11, 12, 13, 14]. However, in this wavelength region the transitions in H_2 and D_2 are largely dominated by the Fulcher- α $d^3\Pi_u(v' = 0) \rightarrow a^3\Sigma_g^+(v'' = 0)$ band. The excitation threshold for the $d^3\Pi_u$ state is 13.9 eV for both H_2 and D_2 [12, 15].

In a recent paper, Aguilar *et al* [14] studied the spectra of H_2 with a spectrometer and reported the cross sections of ro-vibrationally isolated lines for an incident electron energy of 20 eV. Their data indicates that the brightest hydrogen line in our filter bandpass is the $Q(1)$ transition with a cross section of 0.77×10^{-19} cm². Labeling of the branches is done using the total orbital angular momentum quantum number N of the final state for Hund's case (b), e.g. $P(N'')$, $Q(N'')$ and $R(N'')$. (For the P -branch, $\Delta N = N' - N'' = -1$; for the Q -branch, $\Delta N = 0$; for the R -branch, $\Delta N = 1$.) The $Q(1)$ transition provides $\sim 50\%$ of the total measured emission. Other significant contributions come from the $Q(2,3)$ and $R(0,1,2)$ lines. For D_2 , significant contributions come from the $P(2,3)$, $Q(1,2,3,4)$ and $R(0,1,2,3)$ lines [11, 13].

The appreciable values of circular polarization for both H_2 and D_2 shown in the lower panel of Fig. 2 indicate that significant transfer of spin-to-orbital angular momentum is achieved for these molecules. The earlier $-P_3/P_e$ data for H_2 appears low when compared with the current results; we attribute this to the fact that the earlier measurements were taken at a higher pressure (12 mTorr *vs* 0.5 mTorr) and in the presence of a 10^{-2} T magnetic field [5]. Direct comparison of the H_2 and D_2 values is problematic due to the fact that several rotational states are contributing to the measured fluorescence, and the different states will generally exhibit varying degrees of

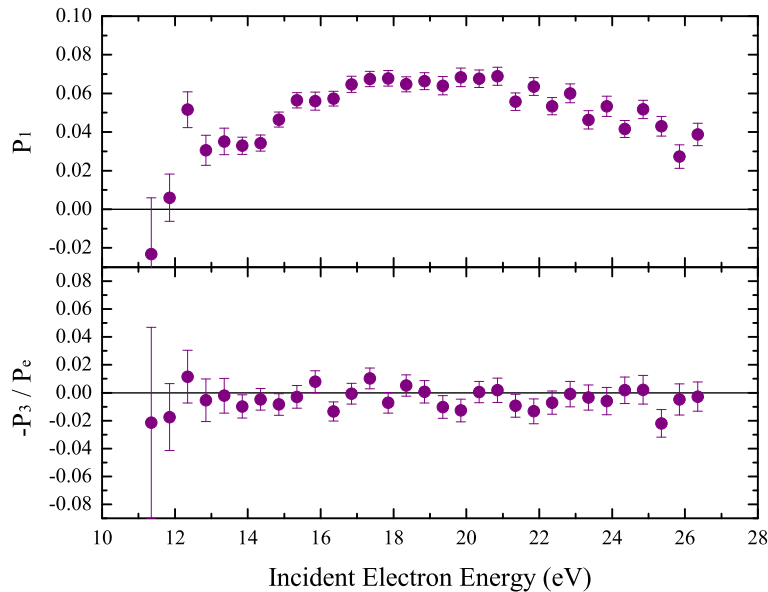


Figure 3. Linear and circular polarization fractions (P_1 and $-P_3/P_e$) for the second positive band in N_2 . Data was acquired at a pressure of 0.3 mTorr with a 380.1 nm (3.5 nm FWHM) bandpass filter.

polarization. However, this data does represent a lower bound for $-P_3/P_e$ values from the individual lines with the largest circular polarizations. We are presently preparing a study of the Stokes parameters from several rotationally-resolved states in H_2 and D_2 .

4. Linear and circular polarizations from N_2

Given that fluorescence from H_2 and D_2 was found to possess a non-zero circular polarization component, we set out to confirm the previously mentioned null values obtained by the Münster group for the second positive system in N_2 . We have measured the ($v' = 0, v'' = 2$) vibrational band whereas the Münster group investigated the ($v' = 0, v'' = 0$) band, but we do not expect this difference in vibrational quantum numbers to significantly affect the Stokes parameters. The process is

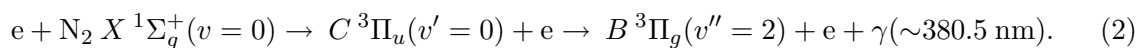


Figure 3 shows our results for P_1 and $-P_3/P_e$. Our values for the circular polarization confirm those reported by the Münster group [3]. The energy-averaged value of $-P_3/P_e$ is -0.004 ± 0.002 .

To understand why the circular polarization is zero, a consideration of the measured rotational transitions is in order. For this experiment, the interference filter bandpass (380.1 ± 3.5 nm FWHM) transmitted all the rotational lines (populated at room temperature, $J_{max} \sim 25$), with only a slight discrimination of R -branch intensities corresponding to large J . Figure 4 depicts the spectrum as computed following the method described in Ref. [16], using the updated C and B state molecular constants reported in Ref. [17]. The upper panel shows the wavelength dependence of the $P(J'')$ -, $Q(J'')$ - and $R(J'')$ -branches. The branches have three sub-branches, corresponding to $^3\Pi_0 \rightarrow ^3\Pi_0$, $^3\Pi_1 \rightarrow ^3\Pi_1$ and $^3\Pi_2 \rightarrow ^3\Pi_2$ transitions (the $^3\Pi_0 \rightarrow ^3\Pi_0$ Q -branch is forbidden [20]). The lower panel shows the intensities as a function of wavelength, and for this plot the transmission profile of the optical filter we used has been taken into account.

Hanne has pointed out that orientation of S cannot lead to orientation of J for the Hund's case (a) situations where $\Omega = 0, 1$ (see Figs. 1.4 and 1.5) [18]. Thus, no circular polarization can be produced from the Hund's case (a) $^3\Pi_0 \rightarrow ^3\Pi_0$ and $^3\Pi_1 \rightarrow ^3\Pi_1$ sub-bands. However, orientation of J can be achieved for the case where $\Omega = 2$, thus non-zero P_3 was expected [3]. (Due to spin uncoupling, or the transition of the C and B states from Hund's case (a) to Hund's

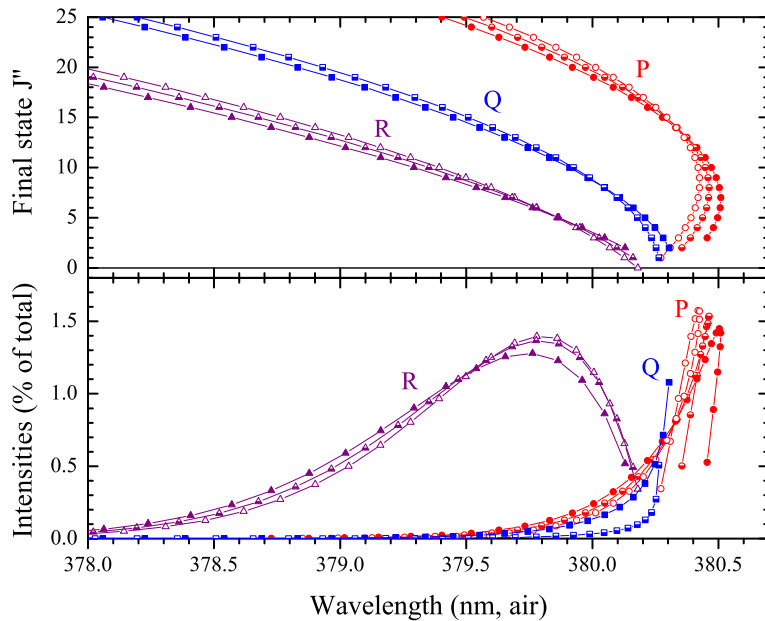


Figure 4. Upper panel: $P(J'')$, $Q(J'')$ and $R(J'')$ branches for the N_2 second positive $v' = 0 \rightarrow v'' = 2$ system. The empty, half-filled and filled points correspond to the $\Omega = 0, 1, 2$ sub-bands, respectively (see text). Lower panel: Intensities for branch J'' values as computed using the method described in Ref. [16] for room-temperature N_2 . This simplified spectra neglects Λ -doubling and weak $\Delta\Omega \neq 0$ transitions [19].

case (b) with increasing J [20], it is likely that the ${}^3\Pi_0 \rightarrow {}^3\Pi_0$ and ${}^3\Pi_1 \rightarrow {}^3\Pi_1$ sub-bands can contribute non-zero circular polarization as well for large J .) The Q -branches are weak: their relative intensity contributions are only 5% of the total emission. Thus, the measured Stokes parameters are mainly due to the R - and P -branches. The P - to R -branch intensity ratios are ~ 1.3 , meaning they have similar contributions.

We now consider the sign of $-P_3/P_e$ values for P - vs R -branch fluorescence. The definition of P - and R -branches in conjunction with conservation of angular momentum suggests that $-P_3/P_e$ for the P - and R -branches should have opposite signs. For a P -branch transition, ΔJ (or ΔN) = -1 , while the R -branch case has ΔJ (or ΔN) = 1 . The molecular angular momentum \mathbf{J} is oriented due to \mathbf{S} in a direction parallel to that of the spin polarization of the incident electron beam. Figure 5 illustrates an initially oriented \mathbf{J} which yields outgoing photon helicities of opposite sign for the P - and R -branches upon fluorescence. This indicates that the sign of $-P_3/P_e$ should be positive for R -branch transitions and negative for P -branch fluorescence. Our recent study of the Stokes parameters for the first negative system in N_2^+ confirms this concept [7]. For this N_2^+ Hund's case (b) $B \ 2\Sigma_u^+(v' = 0) \rightarrow X \ 2\Sigma_g^+(v'' = 0)$ band, our interference filter isolated the P -branch fluorescence from the R -branch contribution and we measured a non-zero energy-averaged value of $-P_3/P_e = -0.0133(8)$. Furthermore, the angular momentum coupling scheme for the excited and final states closely resembles atomic LS -coupling (compare Figs. 1.1 and 1.2). With the substitution $N \rightarrow L$, we use the formalism for atoms provided in Ref. [21] to compute the threshold circular polarization (neglecting hyperfine depolarization) for the $R(N'' = 0)$ and $P(N'' = 2)$ transitions excited from the $N = 0$ molecular ground state. Doing this results in $-P_3/P_e = 0.29$ for the $R(0)$ case and $-P_3/P_e = -0.16$ for the $P(2)$ line, which again confirms that the circular polarizations from P - and R -branches have opposite signs.

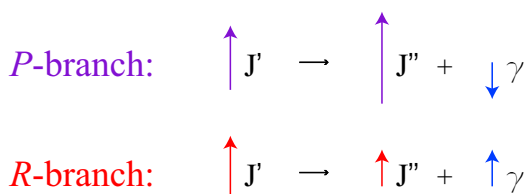


Figure 5. Initially oriented angular momentum \mathbf{J} yielding photons with opposite helicities from the P - and R -branches upon fluorescence.

Returning to the discussion of the circular polarization from the second positive band, the total degree of circular polarization can now be expected to tend towards zero if the magnitude of the P - and R -branch polarizations are similar but have opposite signs, since the total measured fluorescence is comprised of similar amounts of P - and R -branch emission. The relatively large J values in N_2 also play a role in the reduction of observed circular polarization compared to that from H_2 and D_2 . For N_2 , the room-temperature intensity mean occurs at $J \sim 9$, whereas for H_2 $J \sim 1$ and for D_2 $J \sim 2$. Larger J values are less oriented by the electron spin polarization, which leads to smaller values of $-P_3/P_e$. This idea also provides a qualitative explanation as to why the D_2 circular polarization in Fig. 2 is found to be less than that for H_2 . Also, for the H_2/D_2 comparison, D_2 P -branch fluorescence (not seen in the H_2 spectra), which tends to yield negative circular polarization (Fig. 5), should contribute to the reduction of $-P_3/P_e$ values.

5. Conclusion

We have observed significant values of fluorescence circular polarization from Fulcher- α transitions in both H_2 and D_2 excited by spin polarized electron impact. The null circular polarization observed by the Münster group for the N_2 second positive band has been confirmed, and we attribute this effect to rotational-branch averaging. We note that further measurements of the Stokes parameters for the second positive system of N_2 using optical filters to isolate the P - or R -branches, or both, would be useful to confirm the suggested rotational averaging mechanism.

Acknowledgments

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