Alignment and orientation of diatomic molecules induced by polarized electron impact

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Abstract. We report measurements of linear and circular fluorescence polarizations for molecular transitions in H$_2$, D$_2$, and N$_2$ induced by spin-polarized electron impact. Circular polarizations resulting from some Fulcher-α transitions in H$_2$ and D$_2$ 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 N$_2$ to be relatively small compared to those observed from H$_2$ and D$_2$ 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,

\begin{equation}
{\text{e + N}}_2 \ X^1{\Sigma}_g^+ (v=0) \rightarrow C^3{\Pi}_u (v'=0) + \text{e} \rightarrow B^3{\Pi}_g (v''=0) + \text{e} + \gamma (\sim 337.1 \text{ nm}).
\end{equation}

Interestingly, the observed circular polarization (spin-normalized Stokes parameter $P_3/P_e$) was found to be zero at $\sim$14.5 eV within an uncertainty of $2 \times 10^{-3}$. 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 $S$ with the initially unoriented $L$ results in orientation of the total angular momentum $J$ (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
1.1: Atomic $LS$ coupling.

1.2: Hund’s case (b), $\Lambda = 0$.

1.3: Hund’s case (b), $\Lambda = 1$.

1.4: Hund’s case (a), $\Omega = 0$.

1.5: Hund’s case (a), $\Omega = 1$.

1.6: Hund’s case (a), $\Omega = 2$.

**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 $\Sigma$ ($\Lambda = 0$) and $\Pi$ ($\Lambda = 1$) states are shown in (1.2) and (1.3), respectively. Hund’s case (a) situations for $\Pi$ 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].
3. Linear and circular polarizations for H\textsubscript{2} and D\textsubscript{2}

Our results for the linear (Stokes parameter \(P\)) and circular polarizations are shown in Fig. 2. The polarization \(P\) is defined with respect to the electron beam and is independent of the value of \(P\). The spin-normalized circular polarization is reported with a minus sign; this is done to eliminate possible confusion arising from the definition of \(P\), 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\textsubscript{2} and D\textsubscript{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\textsubscript{2} and D\textsubscript{2} are largely dominated by the Fulcher-\(\alpha\) \(d^3\Pi_u(v' = 0) \rightarrow a^3\Sigma^+_g(v'' = 0)\) band. The excitation threshold for the \(d^3\Pi_u\) state is 13.9 eV for both H\textsubscript{2} and D\textsubscript{2} [12, 15].

In a recent paper, Aguilar et al [14] studied the spectra of H\textsubscript{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 \(0.77 \times 10^{-19}\) cm\(^2\). 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\textsubscript{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\textsubscript{2} and D\textsubscript{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\textsubscript{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\textsubscript{2} and D\textsubscript{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
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

$$e + N_2 X^1Σ_g^+(v = 0) \rightarrow C^3Π_u(v' = 0) + e \rightarrow B^3Π_g(v'' = 2) + e + γ(\sim380.5 \text{ nm}).$$

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 $-0.004 \pm 0.002$.

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 ($380.1 \pm 3.5 \text{ nm FWHM}$) transmitted all the rotational lines (populated at room temperature, $J_{\text{max}} \sim 25$), 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 $^3Π_0 \rightarrow ^3Π_0$, $^3Π_1 \rightarrow ^3Π_1$ and $^3Π_2 \rightarrow ^3Π_2$ transitions (the $^3Π_0 \rightarrow ^3Π_0 Q$-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 $Ω = 0, 1$ (see Figs. 1.4 and 1.5) [18]. Thus, no circular polarization can be produced from the Hund’s case (a) $^3Π_0 \rightarrow ^3Π_0$ and $^3Π_1 \rightarrow ^3Π_1$ sub-bands. However, orientation of $J$ can be achieved for the case where $Ω = 2$, 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
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 $\sim 1.3$, 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, $\Delta J(\Delta N) = 0$ transitions [19]. This simplified spectra neglects $\Lambda$-doubling and weak $\Delta \Omega \neq 0$ transitions [19].

![Figure 4](image-url)

**Figure 4.** Upper panel: $P(J''')$, $Q(J''')$ and $R(J''')$ branches for the $N_2$ second positive $\nu' = 0 \rightarrow \nu'' = 2$ 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 $\Lambda$-doubling and weak $\Delta \Omega \neq 0$ transitions [19].

![Figure 5](image-url)

**Figure 5.** Initially oriented angular momentum $J$ yielding photons with opposite helicites 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 $\text{N}_2$ also play a role in the reduction of observed circular polarization compared to that from $\text{H}_2$ and $\text{D}_2$. For $\text{N}_2$, the room-temperature intensity mean occurs at $J \sim 9$, whereas for $\text{H}_2$ $J \sim 1$ and for $\text{D}_2$ $J \sim 2$. 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 $\text{D}_2$ circular polarization in Fig. 2 is found to be less than that for $\text{H}_2$. Also, for the $\text{H}_2/\text{D}_2$ comparison, $\text{D}_2$ $P$-branch fluorescence (not seen in the $\text{H}_2$ 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 $\text{H}_2$ and $\text{D}_2$ excited by spin polarized electron impact. The null circular polarization observed by the Münster group for the $\text{N}_2$ 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 $\text{N}_2$ using optical filters to isolate the $P$- or $R$-branches, or both, would be useful to confirm the suggested rotational averaging mechanism.

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