Threshold Alignment Reversal and Circularly Polarized Fluorescence in Rotationally Resolved \( \text{H}_2 \)

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Using \( \text{H}_2 \) and \( \text{D}_2 \) targets, we have measured the polarization of Fulcher-band fluorescence resulting from spin-polarized electron-impact excitation of vibrationally and rotationally resolved \( ^3\Pi_u \rightarrow a^3\Sigma^+_u \) transitions for incident electron energies from 14.3 to 28.5 eV. Near threshold, the linear polarization \( P_1 \) descends from positive values through zero to negative values, indicating a dynamic production of \( M_N = 0 \) states. The circular polarization \( P_3 \) is measured to be nonzero, indicating the orientation of rotationally resolved molecular states. For \( Q \)-branch transitions, \( P_3 \) is consistent with theory based on Hund’s case (b) coupling. The \( R \)-branch \( P_3 \) values do not agree with theory equally well, indicating the effect of \( \Sigma \)-symmetry perturbation of the parent \( ^3\Pi_u \) state.

Experiments studying electron-impact excitation of atoms and molecules, such as the Franck-Hertz experiment [1], played a crucial role in the early development of the quantum theory. As experiments became more sophisticated, well-defined beams of electrons with precisely known energies striking targets in single-collision conditions yielded ever-more detailed information about the many-body collision dynamics of electron-impact excitation and/or fragmentation. Today’s sophisticated experiments, involving various combinations of high energy resolution, multiple particle detection, fluorescence and particle polarization analysis, and spin-polarized constituents, can provide highly detailed information about individual collisions [2,3]. Experiments have advanced in step with improvement to both computational and analytical theory to the point where it is reasonable to assert that quantum theory and occasioned much theoretical work to understand such anomalous threshold values emerged. While the correct kinematic limit is required by quantum mechanics, this restriction holds only as the excess energy above threshold goes to zero. Essentially all extant anomalous results can be understood in terms of inadequate experimental energy resolution, near-threshold temporary negative-ion resonances, or both [9–12].

In the case of molecular targets, the situation is very different. There exists, to our knowledge, only one previous study of threshold polarization for well-defined...
measurements is shown in Fig. 2 of Ref. [14], and a energy width of less than 0.4 eV and a polarization 785 nm laser light. Photoelectrons from this source have electron affinity (NEA) GaAs with circularly polarized spin-polarized electrons by irradiating unstrained negative is given there. Briefly, we obtain a beam of transversely P(c) Signs of to change the collision energy. A lens above the target cell from the field-free target gas cell, whose potential is varied 27% MN target coupling but to the direct dynamic excitation of have a negative limit at threshold due not to kinematic We also find that with molecules the linear polarization can a pure Hund’s case (b) coupling of three angular momenta. These data match well with our theoretical predictions for lar momentum quantum numbers are completely known. by electron impact of target molecular states whose angu-

FIG. 1 (color online). The classical dynamics of threshold excitation for both atoms and molecules (see text). (a) S → P atomic excitation showing the P-state M_f orbitals. The direction of the incident electron momentum k_e, which is the same as the momentum transfer at threshold, is indicated. The 0, +, and − signs indicate the sign of P_1 produced when the respective M_f states decay. (b) Σ → Σ or Σ → Π molecular excitation for N = 1. Various nuclear rotational orientations at a given instant are shown, with the electronic state that can be excited for purely longitudinal momentum transfer. The dashed circles represent the nuclear orbitals over time. Unlike the atomic threshold case, molecular Π-state excitation can yield M_N = ±1 and 0. (c) Signs of P_1 for Π-state emission. The arrows indicate the classical direction of N.

excited states [13]. In this Letter, we present systematic measurements of fluorescence polarization from rotationally and vibrationally resolved states of the fundamental H_2 system. By using an incident spin-polarized electron beam, we have succeeded in observing orientation induced by electron impact of target molecular states whose angular momentum quantum numbers are completely known. These data match well with our theoretical predictions for a pure Hund’s case (b) coupling of three angular momenta. We also find that with molecules the linear polarization can have a negative limit at threshold due not to kinematic target coupling but to the direct dynamic excitation of M_N = 0 states.

The experimental apparatus we used to perform these measurements is shown in Fig. 2 of Ref. [14], and a detailed discussion of our basic experimental procedure is given there. Briefly, we obtain a beam of transversely spin-polarized electrons by irradiating unstrained negative electron affinity (NEA) GaAs with circularly polarized 785 nm laser light. Photoelectrons from this source have an energy width of less than 0.4 eV and a polarization P_e = 27%. A differential pumping region separates the source from the field-free target gas cell, whose potential is varied to change the collision energy. A lens above the target cell images light from excited molecules into an optical polarimeter, comprising a rotatable quarter-wave retarder, linear polarizer, optical bandpass filter, and a cooled Hamamatsu R946 photomultiplier tube. We use individual, very narrow (0.14 nm FWHM) interference filters for wavelengths 600.7, 601.8, 618.3 nm, 622.5, and 623.8 nm, to isolate each of the molecular rotational transitions of interest: D_2 Q(3)[0], H_2 Q(1)[0], H_2 R(1)[2], H_2 Q(1)[2], and H_2 Q(3)[2], respectively, where the number in square brackets is both the excited-state and final-state vibrational quantum number. In the Q(N) transitions, the initial, excited, and final states have nuclear rotational quantum number N. In all cases, the total nuclear spin is I = 1. These transitions were picked to be well separated from other, spectrally dense transitions of the Fulcher band.

Our data are shown in Figs. 2 and 3. Figure 2 focuses on P_1 for the H_2 Q(1) transitions, for which there exist other theoretical and experimental data for comparison. Figure 3 shows all of our polarization data, including those for the circular polarization fraction P_{c}, which is proportional to the electron spin–induced magnetic dipole moment of the excited molecular states [5].

We comment first on some general features of the data. Our P_1 results displayed in Fig. 2, while in qualitative agreement with previous experimental values [13,15,16], are in qualitative disagreement with theory [17]. Our data in Figs. 2 and 3 decrease monotonically toward zero as the threshold energy is approached, and some transitions reach negative values for the lowest energies. In addition to the data of Ref. [13] and that for rotationally unresolved transitions in N_2 [18,19], these are the only data of which we are aware that exhibit this behavior, with the caveats that the collisions involve simple excitation without fragmentation and are unperturbed by the presence of obvious negative-ion resonances. We note that a few atomic systems [7,9,20] exhibit this behavior, but do so as required by

FIG. 2 (color online). Linear polarization fraction P_1 as a function of incident electron energy for excitation of the Q(1) transition. The present rotationally resolved results are compared with our previous measurements with a wider bandwidth filter [18] and data from other groups [13,15,16]. Also shown are the theoretical predictions of Meneses et al. [17].
target coupling kinematics and/or in the presence of strong resonances. While it is possible that our results are affected by rovibrational f-band resonances in the vicinity of 14–15 eV [21], we see no evidence for such features in our excitation functions or in the energy dependence of \( P_1 \) or \( P_3 \). The behavior of \( P_1 \) is featureless from threshold to 28.5 eV, well above the range of such resonances. Moreover, we could find no reports for decay of these resonances into \( d^3\Pi_u \) states; their major decay channels appear to be into \( C^1\Pi_u \) and \( c^3\Pi_u \) states [21].

In considering just our rotationally resolved \( P_1 \) data in both Figs. 2 and 3(a), it is apparent that, with the exception of the \( D_2 \) results, they reach negative values for energies closest to threshold. The data of Cahill et al. do not, and we have no explanation for this. We point out, however, that their interference filter had a FWHM bandpass of 0.8 nm, compared with our filter’s 0.14 nm bandpass, and that Fulcher-band transitions in the vicinity of 622–623 nm are spectrally dense [22]. Our rotationally unresolved data, taken with a 10 nm bandpass filter (Fig. 2), do not reach negative \( P_1 \) values, although they are certainly trending in this direction.

The cause of these negative values, and the basic physics underlying this novel threshold behavior, can be understood classically for the case of \( Q(1) \) transitions with the help of Figs. 1(b) and 1(c). Unlike the atomic case, the threshold restriction that the momentum transfer be along the \( z \) axis allows for either \( \Pi \) or \( \Sigma \) states with \( M_N = 0 \) or \( \pm 1 \) to be excited. For the case of \( \Pi \) excitation, this can only happen when the target’s internuclear axis is perpendicular to \( z \). When an excited \( \Pi \) state decays, it emits light with \( P_1 \geq 0 \) if \( M_N = \pm 1 \), and \( P_1 \leq 0 \) if \( M_N = 0 \); this is the opposite of the case for \( P \rightarrow S \) atomic fluorescence. Thus, the negative sign of \( P_1 \) in our measurements at threshold indicates a slight dynamical preference for excitation of states with \( M_N = 0 \). This is somewhat surprising, given that the ground state \( (N = 1, M_N = \pm 1) \) sublevels are twice as common as those with \( M_N = 0 \), and can only be excited to \( \Pi \) states at threshold, whereas the \( M_N = 0 \) states can be excited to either \( \Pi \) or \( \Sigma \) states. This result also disagrees with the calculations of Meneses et al. [17], in which the excitation of \( \Pi \) states with \( M_N = 0 \) vanishes at threshold. We note, however, that the symmetry arguments of Dunn [23], invoked in Ref. [17], do not forbid \( P_1 < 0 \).

The nonzero \( P_3 \) values shown in Fig. 3(b), which are relatively insensitive to the incident beam energy, represent the observation of orientation for rotationally resolved molecular states. Earlier electron-\( H_2 \) 601.8 nm photon coincidence experiments by McConkey et al. [15] attempted to observe a nonzero \( P_3 \) caused by the breakdown of axial collision symmetry, but their statistical accuracy was insufficient to achieve this goal. This illustrates the principle that sometimes angle-averaged experiments, while losing information related to specific momentum transfer, can provide new, related information because of their higher count rates. Finally, we note that, for a given rotationally resolved transition, the data of Figs. 2 and 3 are essentially independent of vibrational quantum number and isotopic composition.

We now attempt to explain the above observations more quantitatively using the formalism of state multipoles [5,6]. For unpolarized electrons, early work on this problem was carried out by Blum and Jakubowicz [24]. They showed that a nonzero \( P_1 \) can be measured due to the alignment created in the orbital angular momentum (electrons plus nuclei) \( N \) system. Over time, however, this initial alignment is decreased via fine-structure and hyperfine-structure depolarization due to coupling with the electronic (\( S \)) and nuclear (\( I \)) spins.

If spin-polarized electrons are used, the situation becomes more complicated. In the present case, the spin polarization of the electrons is transferred to the \( S \) system of the excited \( ^3\Pi_u \) state via electron exchange. From there, spin-orbit interactions lead to a partial transfer of this polarization to the \( N \) and \( I \) systems. The observed value of \( P_3 \) is ultimately due to the orientation of \( N \).

Depolarization effects can be treated with the formalism of “generalized perturbation coefficients” using coupled state multipoles for three systems: \( N \), \( S \), and \( I \) [25,26]. In \( H_2 \) and \( D_2 \), Hund’s case (b) coupling is a reasonable
starting point, since \( N = \Lambda + \mathbf{R} \) (where \( \Lambda \) is the projection of the electronic orbital angular momentum on the internuclear axis and \( \mathbf{R} \) is the nuclear rotational angular momentum) is a good quantum number. In this scheme, \( N + S \to J \) and \( J + I \to F \). However, since \( J \) and \( F \) are not good quantum numbers for the \( d^3 \Pi_u \) state [27], one may ultimately need to consider other coupling schemes [6,24]. Note that relatively simple results can only be derived if all fine- and hyperfine-level splittings are large compared with the fluorescence linewidth \( \gamma \). Since this is true in the present case, full depolarization of \( S \) occurs.

The time-averaged multipole moments of the excited molecular system are expressed as [25]

\[
\langle T^+_{KQ}(N) \rangle = \sum_{K'Q'K'Q} \langle T^+_N(N) \rangle \langle t^+_{K'Q'} \rangle G^{Q'Q}_{K'K}. \tag{1}
\]

Here, \( \langle T^+_N(N) \rangle \) and \( \langle t^+_{K'Q'} \rangle \) are the initial state multipoles of the \( N \) and \( S \) systems, respectively, while the \( G^{Q'Q}_{K'K} \) are the generalized perturbation coefficients. We absorb a factor \( \sqrt{1/2J+1} \), i.e., the monopole term from the unpolarized nuclear system, into \( G^{Q'Q}_{K'K} \) below. In addition to the monopole terms \( \langle T^+_N(N) \rangle \langle t^+_{K'Q'} \rangle \), the only parameters that enter the relevant equations for dipole radiation are the alignment \( \langle T^+_N(N) \rangle \) and spin orientation \( \langle t^+_{K'Q'} \rangle = iP_e/3 \) [28].

In our notation, and for our special case of an initially unpolarized nuclear spin system, the generalized perturbation coefficients are given by

\[
G^{Q'Q}_{K'K} = \sqrt{\frac{(2K'+1)(2K+1)}{2(2S+1)(2I+1)^2}} \sum_{S-J-Q} (-1)^{N-S-J-Q} \times (2J+1)^2 \left( \begin{array}{ccc}
N & J & S \\
K' & K'
\end{array} \right) \left( \begin{array}{ccc}
Q' & -Q \\
J & N & K
\end{array} \right) \times \left( \begin{array}{ccc}
N & S & K \\
K' & K'
\end{array} \right) \sum_{F} \left( \begin{array}{ccc}
F & F & K \\
J & I & J
\end{array} \right)^2. \tag{2}
\]

We can now calculate \( P_1 \) and \( P_3 \) using Eqs. (4.6.10), (4.6.11), and (6.1.1) from Ref. [5]. All results can be expressed in terms of the relative alignment parameters \( A_{20}(N) = \langle T^+_N(N) \rangle / \langle T^+_0(N) \rangle \) and \( A_{11} = \langle T^+_1(N) \rangle / \langle T^+_0(N) \rangle \). For the various transitions considered here, we obtain

\[ Q(1): \quad P_1 = \frac{0.061A_{20}(1)}{1 + 0.020A_{20}(1)}, \tag{3} \]

\[ R(1): \quad P_1 = \frac{0.195A_{20}(2)}{1 - 0.065A_{20}(2)}, \tag{4} \]

\[ Q(3): \quad P_1 = \frac{0.321A_{20}(3)}{1 + 0.214A_{20}(3)}. \tag{5} \]

with

\[ A_{20}(1) = \sqrt{2}(\sigma_1 - \sigma_0)/\sigma(N = 1), \]

\[ A_{20}(2) = \sqrt{10/7}(2\sigma_2 - \sigma_1 - \sigma_0)/\sigma(N = 2), \]

\[ A_{20}(3) = \sqrt{1/3}(5\sigma_3 - 3\sigma_1 - 2\sigma_0)/\sigma(N = 3). \]

Here, \( \sigma_m \) are magnetic sublevel cross sections, and \( \sigma \) is the angle-integrated cross section.

Consequently, the observable value of \( P_1 \) must lie between particular limits. The extreme cases occur when \( \sigma_0 \) or \( \sigma_{m_{max}} \) dominates the excitation process. The ranges are

\[ Q(1): \quad -8.9\% \leq P_1 \leq +4.3\%, \tag{9} \]

\[ R(1): \quad -21\% \leq P_1 \leq +25\%, \tag{10} \]

\[ Q(3): \quad -49\% \leq P_1 \leq +35\%. \tag{11} \]

The formula and the limit for the \( Q(1) \) transition were also derived by Meneses et al. [17]. The small difference between our range and theirs is due to their (incorrect) value of \( G_0 = 0.964 \) instead of 1. The energy dependence of their theoretical prediction for \( P_1 \) is due entirely to their dynamical calculation of the various \( \sigma_m \).

In the formula for \( P_3 \), \( A_{20} \) only appears in the denominator, i.e., in the expression for intensity. Our experimental results for \( P_1 \) show that the influence of the term with \( A_{20} \) is small, either because \( |A_{20}| \) is small itself or, as for the \( Q(1) \) transition, because strong depolarization results in a small perturbation coefficient.

With this assumption, the result for \( P_3 \) depends only on \( A_{11} \). The latter parameter is constructed from \( \langle T^+_0(N) \rangle \), \( \langle T^+_2(N) \rangle \), and \( \langle t^+_{11} \rangle = iP_e/3 \). Since \( G^{011}_{211} \ll G^{011}_{011} \) in all cases, the term with \( \langle T^+_2(N) \rangle \) can be neglected as well. Since the only remaining parameter that depends on the dynamics, \( \langle T^+_0(N) \rangle \), cancels out in the formula for the circular polarization, the circular polarization \( P_3 \) is directly proportional to the electron spin polarization, with the proportionality factor given by combinations of \( 3j \), \( 6j \), and \( 9j \) symbols. We obtain the following:

\[ Q(1): \quad P_3/P_e = -18.7\%, \tag{12} \]

\[ R(1): \quad P_3/P_e = -29.5\%, \tag{13} \]

\[ Q(3): \quad P_3/P_e = -5.3\%. \tag{14} \]

As seen in Fig. 3, the predictions for the \( Q(N) \) transitions are in satisfactory agreement with the measurements. The \( R(1) \) experimental results are, however, consistently below theory. We speculate that this is because the \( d^3 \Pi_u^+ \) state, the parent for \( R(1) \) fluorescence, is significantly perturbed by the \( d^3 \Sigma_u^+ \) state [16,27]. This extra \( \Sigma \) character of the wave function should reduce its overall orientation. In general, we note again that neither \( J \) nor \( F \) is a good quantum number in the \( d^3 \Pi_u^+ \) state. Thus, pure Hund’s
case (b) coupling may need to be replaced in a more rigorous approach by an intermediate coupling scheme developed from a calculation of the molecular hyperfine dynamics [6,24,27].

In summary, the present data point out the qualitatively different physics between atoms and molecules in near-threshold excitation. We have observed a change near threshold in the sign of molecular fluorescence polarization (alignment) due to the dynamical energy dependence of the various magnetic substate cross sections, as opposed to variation caused by target coupling or resonance effects. Moreover, we have observed circularly polarized fluorescence polarization from rotationally and vibrationally resolved excited target states resulting from their orientation induced by exchange excitation with spin-polarized electrons. These measurements represent a systematic set of benchmark data for electron-molecule scattering, which will hopefully stimulate further theoretical development in the study of electron-molecule collisions.

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