EXCITATION OF THE WERNER BANDS OF H₂ BY ELECTRON IMPACT

BY

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Excitation of the Werner Bands of H₂ by Electron Impact

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Abstract

Absolute cross sections for the excitation of the Werner band system H₂(C¹Πₜ → X¹Σ⁺ₘ) have been measured from energy threshold to 300 eV for electron impact on H₂. The bands were observed in emission in the wavelength region 1100Å - 1250Å. The measured cross sections were compared with published transition probabilities, leading to the conclusion that the Werner bands are suitable as the basis for a relative spectral response calibration only when the bands are observed under sufficiently high resolution (FWHM ~ 0.4Å). The effect of the perturbation between the C¹Πₜ and B¹Σ⁺ₘ states of the hydrogen molecule was clearly observed in anomalies in the rotational intensity distribution in bands of the (3, ν") progression.
INTRODUCTION

The Werner band system of molecular hydrogen \([C^1\Pi_u \rightarrow X^1\Sigma^+_g]\) is readily excited by electron impact,

\[
e + \text{H}_2(X^1\Sigma^+_g) \rightarrow \text{H}_2(C^1\Pi_u) + e.
\]

(1)

\[
\text{H}_2(C^1\Pi_u) \rightarrow \text{H}_2(X^1\Sigma^+_g) + h\nu
\]

The resulting vacuum ultraviolet bands appear as prominent emission features in the wavelength region 800Å - 1400Å. The Werner system is particularly intense from 1100Å to 1250Å where it is accessible to optical instruments using lithium fluoride windows. In this wavelength region the Werner bands are reasonably free from spectral contamination and can generally be distinguished by a monochromator with a modest bandwidth (0.5Å FWHM) from the overlapping hydrogen Lyman bands \((B^1\Sigma_u^+ \rightarrow X^1\Sigma^+_g)\), which are relatively weak. Hence, it is tempting to use the relative intensities of the Werner bands excited by electron impact to determine the spectral sensitivity of an ultraviolet optical system in the 1100Å - 1250Å region. Such measurements can be used in principal to augment atomic branching-ratio data\(^1\) and to extend the molecular branching-ratio techniques based on the LBH system of \(N_2\)\(^2\) to shorter wavelengths.

Calibration experiments of this kind have been carried out by Carriere and de Heer\(^3\), and by Aarts and de Heer\(^4\). In both of these studies the resulting spectral response curves showed a pronounced
dip near 1200Å. These calibration experiments involved measurements made at relatively low resolution, inviting contamination by Lyman-band radiation. This may account for the structure observed in these calibration curves.

There are, however, additional difficulties that complicate the use of the Werner bands in molecular branching-ratio measurements that should also be noted. Dieke\(^5\) first pointed out that the levels of the \(\text{C}^1\Pi_u\) state of the hydrogen molecular are perturbed by nearby levels of the \(\text{B}^1\Sigma^+_g\) state. The effect of these perturbations on line positions has been analyzed by Monfils\(^6\) and treated both experimentally and theoretically by Namioka\(^7\). Julienne\(^8\) has calculated the extent of the mixing of some of the more strongly perturbed levels and his work shows that this mixing leads to significant intensity anomalies. Another complicating factor in the study of the Werner bands is the fact that the \(\text{C}^1\Pi_u\) state is populated to some extent by cascade transitions from more energetic states. These transitions have been discussed by Richardson\(^9\) and Dieke\(^5\), but little is known quantitatively about the extent of the cascade process and its effects on an optical calibration experiment.

In this paper we describe an experiment that clarifies most of these points and shows under what conditions the Werner band system can be used in absolute calibration work. The intensity perturbations predicted by Julienne have been observed, and the absolute cross sections
for electron-impact excitation of the Werner bands are presented. These results are of direct importance in the study of the ultraviolet spectra of the Jovian planets and of the interstellar medium.

**EXPERIMENTAL TECHNIQUES**

The apparatus used in this work is nearly identical to that described in detail by Mumma and Zipf\textsuperscript{10,11}. Hydrogen gas flowed into a small collision chamber located in a large vacuum chamber which was evacuated by two 1400 l/sec diffusion pumps (Figure 1). An electron gun provided a monochromatic beam of electrons whose energy could be varied from 5 to 340 eV. The electron beam passed through the gas in the collision chamber and was collected by a positively-biased electron trap on the opposite side. The current to the electron trap, as well as stray currents to the top, bottom, and side wall of the collision chamber were monitored. Checks were made to ensure that effects due to secondary and reflected electrons were negligible. The resulting radiation was observed through windowless apertures with a one-meter, normal incidence vacuum monochromator and a solar-blind photomultiplier which was operated in a pulse-counting mode. The gas pressure in the collision chamber was monitored by measuring either the pressure in the gas flow line or the background pressure in the large vacuum chamber, and was maintained nearly constant by manual adjustment of the inlet leak valve. Variations due to drifts of various sorts were averaged by taking intensity measurements in repeated sequences.

The relative spectral response of the optical system was determined by the method of hydrogen deuteride fluorescence described by Becker et al\textsuperscript{12}. 


An argon light source with a lithium fluoride window was placed one inch from the optic axis, as shown in Figure 1. The large vacuum chamber was filled with HD to a pressure of few millitorr, and HD fluorescence was observed by the monochromator through an aperture in the back side of the collision chamber. Thus the photon collection geometries in the fluorescence and electron-impact experiments were virtually identical.

The resulting spectral response curve, together with the data points on which it is based, is presented in Figure 2. The ordinate of the graph is the ratio of observed intensity to the predicted intensity. The solid line is a computer-generated least-squares third order fit to several sets of data.

The rotational line intensities of individual Werner bands were measured by scanning the monochromator slowly over the line with the slits set to achieve a resolution of 0.44 Å. For each band, the intensity of the Q1 line was measured and taken as representative of the intensity of the whole band. This procedure was adopted for several reasons. The Q1 line is the strongest single feature in each band, and is well isolated from other rotational lines of the same band. Furthermore the Q-branch lines originate on levels of the C state which, due to their symmetry, are not subject to perturbation by levels of the B state. No attempt was made to integrate measured intensity over an entire Werner band, since doing so would have resulted in serious errors due to contamination by Lyman radiation and irrelevant rotational lines from overlapping Werner bands in the same spectral region. The problem of contamination is not entirely eliminated by confining intensity
measurements to single lines, but it is greatly reduced. The measured rotational intensities were converted into absolute excitation cross sections by comparison with the intensity of Lyman Alpha (1215.6Å) produced in dissociative excitation of H$_2$ by electrons of 100 eV energy. The latter cross section was taken to be 1.2 x 10^{-17} cm$^2$ (see Mumma and Zipf$^{11}$).

Excitation functions for the Werner bands were taken by setting the monochromator slits unequal and wide enough to include the R0, R1, R2, and Q1 lines of each band in the maximum pass band. The excitation function, defined as the number of photons collected per unit time per unit electron current per unit gas pressure within the experimental chamber as a function of electron energy, is thus directly proportional to the excitation cross section as a function of electron energy.

**THEORY**

Probabilities for radiative transitions from the C to the X state of the H$_2$ molecule have been calculated by Allison and Dalgarno$^{13}$. Relative probabilities for electron-impact excitation of the various levels of the C state from the X state may be deduced from these values by invoking the Born and Born-Oppenheimer approximations. In this approximation$^{14}$ a generalized oscillator strength may be defined in the expression for the differential scattering cross section. In the limit that the excitation energy for the transition is small compared to the electron impact energy, this generalized oscillator strength approaches the optical oscillator strength, and it follows that the cross section for electron-impact excitation is directly proportional to the probability of photon absorption from a continuum radiation field. Thus the probability for excitation to the v' vibrational level of the upper state is proportional to
\[ P_{v'} \propto A_{v',0}/v_{v',0}^3 \]  

(2)

where \( A_{v',0} \) is the radiative transition probability between the \( v' \) vibrational level of the upper state and the \( v'' = 0 \) level of the ground electronic state, and \( v_{v',0} \) is the wave number of the corresponding radiation. The intensity of the \((v', v'')\) band seen in emission will then be proportional to

\[ I_{v',v''} \propto P_{v'} \cdot A_{v',v''}/\Sigma_{v''} A_{v',v''} . \]  

(3)

where \( A_{v',v''} \) is the radiative transition probability between the \( v' \) and \( v'' \) vibrational levels of the upper and lower electronic states, respectively. If the C state is populated to a significant degree by cascade transition from higher-lying excited states, the use of the quantity \( P_{v'} \) is not justified, and bands originating on each upper level must be considered separately.

Werner band transition probabilities and predicted band intensities were also calculated from Franck-Condon factors, using published dipole transition moments and the r-centroid approximation. The appropriate formulae are given by Herzberg\(^\text{15}\). Arrays of Franck-Condon factors for the Werner bands have been calculated by Spindler\(^\text{16}\) and by Halmann and Laulicht\(^\text{17}\). These two sets of numbers are based on RKR potential curves, and agree very well. R-centroids for the Werner bands have been calculated by Halmann and Laulicht\(^\text{18}\). The variation of dipole transition moment with internuclear distance was
taken from the work of Wolniewicz. Other published transition moments for the Werner bands include the experimental result of Geiger and Schmoranzer and the theoretical variation obtained by Miller and Krauss.

The treatment of transition probabilities in $H_2$ using Franck-Condon factors and r-centroids must be regarded as somewhat inexact. Calculations have been reported by Halmann and Laulicht and by Villarejo et al, showing that the Franck-Condon factor for a band is not constant, but varies with rotational quantum number. Drake and Nicholls report that the r-centroid approximation may fail for hydrogen. Nevertheless, as we will show later in this paper, the agreement between the experimental measurements and the results of a Franck-Condon calculation is quite good.

The distribution of intensity in the rotational structure of each band was calculated as follows, using the formulation of Herzberg.

The jth rotational level of the ground ($X^1\Sigma^+$, $v'' = 0$) state is populated in proportion to the quantity

$$W_j \cdot B_j = W_j \exp(-B_{v''} j(j + 1) \frac{hc}{KT})$$

where $W_j$, the statistical weight of the level, is 3 or 1 as $j$ is odd or even, $B_{v''}$ is the rotational constant of the $v'' = 0$ rotational level, $h$ is Planck's constant, $c$ is the speed of light, $K$ is Boltzmann's constant, and $T$, the Kelvin temperature, is 295°. Each of the rotational levels of the upper ($C^1\Pi_u$, $v'$) state is lambda doubled. The two parts of its kth rotational level will be populated according to

7
\[ P_k^{(1)} = W_{k+1} S_{k+1}^P B_{k+1} + W_{k-1} S_{k-1}^R B_{k-1}, \]

\[ P_k^{(2)} = W_k S_k^Q B_k, \quad k = 1, 2, 3 \ldots \]

where \( P_k^{(1)} \) are the relative populations of the levels populated in P and R branches, and the \( P_k^{(2)} \) are the relative populations of the levels populated in Q branches. The \( S_k \) are the Honl-London Factors,

\[
\begin{align*}
S_k^P &= k - 1 \\
S_k^Q &= 2k + 1 \\
S_k^R &= k + 2
\end{align*}
\]

except that

\[ S_1^P = S_2^P = S_1^Q = 0. \]

The intensities of lines seen in emission will then be proportional to

\[
\begin{align*}
I_j^P &= S_j^P P_{j-1}^{(1)} / (2j - 1) \quad j = 2, 3, 4 \ldots \\
I_j^Q &= S_j^Q P_j^{(2)} / (2j + 1) \quad j = 1, 2, 3 \ldots \\
I_j^R &= S_j^R P_{j+1}^{(1)} / (2j + 3) \quad j = 0, 1, 2 \ldots
\end{align*}
\]

where, for example, \( I_3^Q \) is the relative intensity of the Q3 line, and
where \( j \) designates the rotational level of the final state.

Julienne and Mies\(^{25}\) have calculated transition probabilities in the \( P \) and \( R \) branches of the Werner bands of \( \text{H}_2 \), and report that the probabilities follow the Honl-London factors only approximately. While it is not clear what error has been incurred in our calculation of \( Q \) branch intensities by the use of the classical Honl-London factors, \( \pm 5\% \) seems to be a reasonable estimate.

**RESULTS**

The observed intensity distribution in the Werner \((1,3)\) and \((2,5)\) bands is shown in Figures 3 and 4. The predicted distribution is shown for comparison; the agreement is seen to be good. However, the distribution of intensity in the \((3, v'')\) bands shows the effect of the perturbation interaction between the \( B \) and \( C \) states of the molecule. Julienne\(^8\) has calculated that the \((v' = 3, j = 1 \text{ and } 2)\) levels of the \( C \) state are 35% and 65% mixed, respectively, with the \((v' = 14, j = 1 \text{ and } 2)\) levels of the \( B \) state. This results in a reduction in the intensity of the \( R0, R1, R2, \text{ and } P3 \) lines of the Werner \((3, v'')\) bands. Figure 5 compares the observed intensity distribution in the Werner \((3,7)\) band with that expected in the absence of the perturbation. The effect of the intensity perturbation is unmistakable: The effect is less marked in the \((3,6)\) band, apparently due to contamination by other VUV radiation.

The excitation functions for the \( v' = 0 \) through \( v' = 4 \) levels of the \( C \) state were measured from threshold to 340 eV. The total intensity observed was the sum of the \( R0, R1, R2, R3, \text{ and } Q1 \) lines. The shapes of these excitation functions were found to be identical within the experimental
error (± 3%), except near threshold. The excitation function curve for the (4,8) band is shown in Figure 6.

The experimental cross section $\sigma(Q_l)$ for the excitation of the $Q_l$ lines of the prominent Werner bands in the spectral region 1100Å - 1250Å by electrons of 100 eV energy are given in Table I. The quantity $(Q_l/\text{total})$ is the fraction of the intensity of the band which appears in the $Q_l$ line. Predicted intensities, arbitrarily normalized and based on the transition probabilities of Allison and Dalgarno\textsuperscript{13}, are given in the column marked A & D. Predicted relative intensities calculated from the Franck-Condon factors of Spindler\textsuperscript{16}, the dipole transition moment of Wolniewicz\textsuperscript{19}, and the $r$-centroids of Halmann and Laulicht\textsuperscript{22} are given in the column marked FC\textsuperscript{0}. The agreement between the measurements and both sets of predicted intensities is good, generally within ± 5%.

DISCUSSION

The authors undertook the present measurements with the expectation of using the Werner-band intensities to determine the relative spectral response of laboratory and rocket-borne VUV optical systems. Our first measurements of the Werner-band rotational line intensities were made at resolutions of 0.88Å and 0.66Å (FWHM). The spectral response curves generated from these measurements contained unexplained structure near 1200Å.

The spectral sensitivity calibration using HD fluorescence techniques was then carried out, demonstrating that the early Werner-band calibration was in error. The calibration experiment using hydrogen
deuteride has a twofold advantage: it has very few uncertainties in principle, and its spectral range overlaps the wavelength region that may be calibrated accurately using the LBH bands of N₂.

It is now clear from these measurements that certain of the Q₁ line intensities, in particular those of the (3,6) and (1,5) bands, were contaminated by other lines of the hydrogen spectrum. Most of the contamination seems to have been eliminated by decreasing the monochromator bandwidth to 0.44 Å.

Cascade excitation of the C state from high-lying states of the hydrogen molecule also seems to be small at the excitation energies used (100 eV and 300 eV) in this experiment and is not a source of significant error. Hence, the composite results of this study show that the Werner-band system can be used effectively as the basis of a molecular branching-ratio calibration of a VUV optical system, but care must be taken to use sufficient instrumental resolution while observing the Werner bands.

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The authors wish to thank Dr. C. Bradley Moore of the University of California (Berkeley) for useful discussions of the technique of the HD calibration.
FOOTNOTES

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<th>Band</th>
<th>( \lambda (Q_1) ) ( \text{\AA} )</th>
<th>( \sigma (Q_1) ) ( 10^{-19}\text{cm}^2 )</th>
<th>( \frac{\sigma (Q_1)}{\text{whole}} )</th>
<th>( \sigma (\text{band}) ) ( 10^{-18}\text{cm}^2 )</th>
<th>A &amp; D</th>
<th>PCF</th>
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Figure Captions

Figure 1  Diagram of the experimental apparatus.

Figure 2  Relative spectral sensitivity of the experimental optics, based on observations of HD fluorescence.

Figure 3  Experimental (histogram) and simple-theory (vertical bars) distribution of intensity in the Werner (1,3) band.

Figure 4  Experimental (histogram) and simple-theory (vertical bars) distribution of intensity in the Werner (2,5) band. The P3 peak is contaminated.

Figure 5  Experimental (histogram) and simple-theory (vertical bars) distribution of intensity in the Werner (3,7) band.

Figure 6  Experimental excitation function for the Werner (4,8) band.
Figure 2
Figure 3

Werner (1, 3) Band

$R_1, R_0, R_2$

$Q_1$

$R_3$

$Q_2, P_2, Q_3$

$P_3$

$H_15$

$H_20 \, \text{Å}$
Werner (2,5) Band

Figure 4
Figure 6