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Molecular Branching Ratio Method for Intensity Calibration of Optical Systems in the Vacuum Ultraviolet

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ABSTRACT

A state-of-the-art review is given of the molecular branching ratio method for intensity calibration in the vacuum ultraviolet. Ways are described for determining both relative and quantitative responses in the wavelength range 1000 Å < λ < 3000Å. The molecular band systems which are discussed are: $H_2(B^1\Sigma_u^+ - X^1\Sigma_g^+)$, $H_2(C^1\Pi_u - X^1\Sigma_g^+)$, $N_2(a^1\Pi_g - X^1\Sigma_g^+)$, $CO(A^1\Pi - X^1\Sigma^+)$, $NO(A^2\Sigma^+ - X^2\Pi_r)$, and $NO^+(A^1\Pi - X^1\Sigma^+)$.

Unitl recently, calibration of optical systems in the vacuum ultraviolet ($1000 < \lambda < 3000\text{Å}$) was extremely difficult. With the exception of the atomic branching-ratio method, the available techniques were not suited to _in-situ_ calibration of an optical system.[1,2] Furthermore, the method of atomic branching ratios gave only a few scattered calibration points over a wide wavelength range and required two optical systems, one to calibrate the long-wavelength atomic line intensity (typically He 5015Å) and one for use in the vacuum ultraviolet (typically He 584Å). For completeness, we mention some of the other calibration procedures that were available or suggested: (1) double-monochromator technique used with a thermopile detector, sodium salicylate detector, or photoionization detector, (2) synchrotron emission, used as a known source with a calculable spectral distribution, and (3) delayed-coincidence atomic line fluorescence[3,4] (e.g. H(3s-2p) 6563Å and H(2p-1s)1216Å). These methods suffered from one or more of the following problems: (1) limited wavelength range, (2) impracticability of _in-situ_ measurements, (3) uncertainty of polarization effects, and (4) self-absorption of atomic lines terminating on the ground electronic state. These problems were largely overcome by the recently developed molecular branching-ratio technique.

The extension of the branching ratio technique to molecular band intensities was suggested independently by McConkey[5] and Aarts and de Heer[6,7] McConkey found good agreement between the spectral response (3000 - 4500Å) measured with an NBS quartz-iodine lamp and the spectral response determined from intensity measurements on the $N_2(C^3\Pi_u - B^3\Pi_g)$ second positive group. Aarts and de Heer measured the relative intensities of bands (1400-2600Å) belonging to the $CO(A^1\Pi - X^1\Sigma^+)$ fourth positive group and the $CO^+(B^2\Sigma^+ - X^2\Sigma^+)$ first negative group. Although they recognized that the electronic transition moment, R_e, might not be constant for the systems, Aarts and de Heer assumed constant R_e for the purpose of deriving a spectral response curve and demonstrating the usefulness of the technique. This early work[5,6,7] demonstrated the feasibility of the method, but the reliability was unknown since the variation of electronic transition moment had not been accurately measured or calculated for any band system ($\lambda < 3000$Å) except $N_2(a^1\Pi_g - X^1\Sigma_g^+)$.

The first quantitative, detailed treatments of the technique in the vacuum ultraviolet were given independently by Mumma and Zipf[8,9] (N_2(a-X) and CO(A-X))and by Becker <u>et al.</u>[10]

(H_2 and HD(B-X)). Further advances have been made by Poland and Broida[11] (NO(A-X)), Stone and Zipf[12,13] (NO^+(A-X) and H_2(C-X)) and Aarts and de Heer[14] (NO^+(A-X)). In this paper, we review the theory and the molecular band systems that may be used for intensity calibration in the vacuum ultraviolet ($1000Å < \lambda < 3000Å$). The method is useful for wavelengths longer than 3000Å as well. Band systems at wavelengths longer than 3000Å have not been included in this review since standard lamps are routinely used for intensity calibration at wavelengths longer than 2600Å.

THEORY

Consider two molecular electronic states that are connected by an electric-dipole-allowed transition. The volume emission rate (photons/cm^3 sec 4πSr) will be given by

$$\beta_{v'v''} = n_{v'} A_{v'v''} \tag{1}$$

where $n_{v'}$ is the number density (cm^{-3}) in level v' and $A_{v'v''}$ is the transition probability (sec^{-1}). If the photons are incident on an optical system (monochromator + windows + detector) which has a spectral sensitivity $R(\lambda)$, then the measured counting rate (counts/sec) for a band (v',v") is given by

$$S_{v'v''} = GR(\lambda_{v'v''})\,\beta_{v'v''}. \tag{2}$$

G is a geometrical function involving the acceptance solid angle of the optical system, source characteristics, monochromator slit settings, etc. G is kept constant for observations of a given band system and is thus of no importance in determining the relative spectral response. The transition probability[15] is given by

$$A_{v'v''} = \frac{64\pi^4}{3h} q_{v'v''} \nu^3_{v'v''} R_e^2(v',v''), \tag{3}$$

where $q_{v'v''}$ is the vibrational overlap integral (Franck-Condon factor), and $\nu_{v'v''}$ is the wave-number (cm^{-1}). The lifetime of the vibrational level v' is $\tau_{v'} = (A_{v'})^{-1}$, where

$$A_{v'} = \Sigma_{v''} A_{v'v''}, \tag{4}$$

and the molecular branching ratio is defined as

$$B.\ R. = A_{v'v''}/A_{v'}. \tag{5}$$

The relative intensities of bands belonging to a v" progression (v' constant) are independent of $n_{v'}$ Eqs. (1,2,3) and depend only on the branching ratios, so that

$$\frac{S_{v'v''_1}}{S_{v'v''_2}} = \frac{R(\lambda_{v'v''_1})q_{v'v''_1}\nu^3_{v'v''_1}R_e^2(v'v''_1)}{R(\lambda_{v'v''_2})q_{v'v''_2}\nu^3_{v'v''_2}R_e^2(v'v''_2)} \tag{6}$$

This means that the relative spectral response of the optical system can always be extracted from measurements of the relative counting rates for a given v'' progression, independent of the ways in which the various v' are populated. Thus, effects such as cascade, quenching, self absorption (except for bands terminating on v'' = 0), and excitation mechanism (e.g. exchange interaction vs direct excitation by electron impact) have no effect on the measured relative spectral response. Hence, the method is readily used in discharge systems, controlled electron beam experiments, and photo-excitation sources. The results for different v'' progressions are best internormalized by requiring a least-squares fit of the data to a third-order expression in λ for $R(\lambda)$ (see Mumma and Zipf[8] for further details). A requirement for using Eq. (6) is that R_e^2 be known for bands (v',v''). A frequently successful approach is to express R_e in terms of the r-centroid, $\bar{r}_{v'v''}$[16,17,18].

Under certain circumstances cascade contributions to the excited state may be negligible. The electron impact cross sections $\sigma_{ov'}$ for direct excitation by a monoenergetic electron beam are given by[15,19]

$$\sigma_{ov'} \alpha\ f_{ov'} \lambda_{ov'}\ \alpha\ \lambda^3_{ov'}\ A_{ov'}$$

$$\sigma_{ov'}\ \alpha\ q_{ov'}\ R_e^2(\bar{r}_{ov'}), \tag{7}$$

at sufficiently high electron energies (typically E > 100 eV), where $f_{ov'}$ is the absorption oscillator strength. For lifetimes $\tau_{v'}$ which are sufficiently short, the molecule essentially radiates _in situ_ and the equilibrium number density, $n_{v'}$, is given by

$$\frac{dn_{v'}}{dt} = 0 = Jn_o \sigma_{ov'} - n_{v'} A_{v'},$$

or

$$n_{v'} = \frac{Jn_o \sigma_{ov'}}{A_{v'}} \tag{8}$$

where J represents the electron beam current density. Then the relative counting rates in the band system are given by Eqs. (1,2,3,7 and 8)

$$\frac{S_{v_1'v_2''}}{S_{v_3'v_4''}} = \frac{R(\lambda_{v_1'v_2''})\; q_{ov_1'}\; R_e^2(\bar{r}_{ov_1'})\; (q\nu^3)_{v_1'v_2''}\; R_e^2(\bar{r}_{v_1'v_2''}) A_{v_3'}}{R(\lambda_{v_3'v_4''})\; q_{ov_3'}\; R_e^2(\bar{r}_{ov_3'})\; (q\nu^3)_{v_3'v_4''}\; R_e^2(\bar{r}_{v_3'v_4''})\; A_{v_1'}} \tag{9}$$

The electronic transition moment usually varies across the band system, but when it is constant Eqs. (6) and (9) reduce to an especially simple form. Accurate Franck-Condon factors and r-centroids are available for many systems. Albritton, Schmeltekopf, and Zare's Rydberg-Klein-Rees calculations[20] are especially useful since their tables include $q, \bar{r}$, and $q\nu^3$.

Excitation of molecular band systems by electron impact at moderately high energies is expected to produce essentially unpolarized radiation since many closely spaced rotational levels are usually excited (exception, H_2, e.g. see Ref. 21). Although a particular rotational line may show polarization effects, rotational averaging is expected to yield a net polarization near zero for the band. This is the case for the NO γ bands.[11] However, when NO γ line fluorescence is excited by level-crossing-spectroscopy, the resultant rotational lines are polarized. Intensity calibration by polarized molecular line fluorescence can give misleading results if the monochromator has a wavelength-dependent polarization.

DISCUSSION OF SPECIFIC BAND SYSTEMS

$H_2(B^1\Sigma_u^+ - X^1\Sigma_g^+)$

Becker, Fink, and Allison[10] have excited single rotational levels in the H_2 B state (v'=3, J'=1) and the HD B state (v'=3, J'=2) by absorption of the Ar 1066.66Å resonance line. The emitted (B-X) radiation consists of one P-branch line and one R-branch line for each transition (3,v"). Thus the H_2 many-line spectrum is reduced to an easily used subset of 28 lines (Table I). The transition probabilities have been calculated ab initio by Allison and Dalgarno[22] and their results were confirmed by the independent calculation of Julienne.[23] Becker _et_ _al_. showed that a calibration curve established using the Lyman lines (1100 - 1650 Å) was in good agreement with similar measurements (1325 - 1800Å) on the $N_2(a^1\Pi_g - X^1\Sigma_g^+)$ Lyman-Birge-Hopfield (LBH) band system in the range of overlap (1325 - 1650Å).

In application, the emitted line intensities are much brighter from HD than from H_2, because the Ar 1066 Å line is in closer resonance with the HD transition and the statistical weight for the ground state level is more favorable. The useful wavelength range is smaller than that indicated in Table V because the (3,0) lines are subject to self absorption and the (3,3), (3,12), and (3,13) lines are quite weak in emission. The practical range over which the Lyman line fluorescence may be used for calibration purposes is thus 1112 - 1638 Å.

$H_2(C^1\pi_u - X^1\Sigma_g^+)$

Aarts and de Heer[24] and Carriere and de Heer[25] first attempted to use the Werner bands for calibration purposes. Their intensity measurements were made at 4Å resolution. This was later shown to be inadequate to eliminate band overlap,[12] giving rise to a pronounced dip in the resultant calibration curve around 1200Å. Such insufficient resolution has led to erroneous values in the literature for dissociative excitation cross sections.

Stone and Zipf[12] have recently investigated the use of Werner bands for intensity calibration. They find that a spectral resolution of 0.44Å is required to eliminate most of the problems produced by overlapping lines. The lines of the P and R branches are known to be subject to strong perturbations due to mixing of the B' $^1\Sigma_u^+$ and $C^1\pi_u$ states. The Q-branch lines are not subject to this perturbation since the symmetries of the C rotational levels that generate the Q-branch are different from the symmetries of the corresponding B' levels. The Q1 lines are mainly free from overlap by P and R branch lines. Stone finds that their observed intensities are in close agreement ($\pm$3%) with the theoretical intensities calculated by two methods, (1) Eq. (6) and the ab initio transition probabilities of Allison and Dalgarno[22], and (2) Eq. (9) and the appropriate Franck-Condon factors and electronic transition moments.

The relative emission intensities for Q1 lines have been calculated using Eq. (6) and the transition probabilities of Allison and Dalgarno and are presented along with the appropriate wavelengths in Table II. To date, only Q1 lines in the range 1100-1250Å have been experimentally verified to follow these intensity relations. The prospective user is cautioned to check for overlap by P and R Branch lines.

$$N_2(a^1\pi_g - X^1\Sigma_g^+)$$

The LBH band system of N_2 consists of compact (full width at half maximum (FWHM) < 2Å) single headed bands (1275 - 2100Å) which are readily excited by electron impact. The electronic transition (a-X) is forbidden by electric dipole interaction and proceeds mainly by magnetic dipole interaction although there is some electric quadrupole contribution as well.[26] McEwen[27] was the first to investigate quantitatively the emission intensities of these bands; he established that R_e was constant to within $\pm 20\%$. McEwen's intensity calibration was based on the constant quantum yield of sodium salicylate over the wavelength range in question. Subsequent investigations by numerous authors have found no variation of R_e. Holland[28] observed the emission intensities with an optical system which had been calibrated using the double-monochromator technique and a thermopile detector. Lassettre[29] used the electron-energy-loss method to show that the excitation cross sections, $\sigma_{ov'}$, followed the Franck-Condon factors for v'=o through v'=12. Mumma[8,30] used atomic nitrogen (NI) branching ratios to verify that R_e was constant. Ajello[31] measured the band emission intensities using an optical system that was calibrated by use of the double-monochromator method and a sodium salicylate detector. A curve-of-growth analysis[32] also indicated a constant R_e, but these data covered a very limited range of r-centroids and the results are not indicative of the whole band system.

The lifetime of the $a^1\pi_g$ state is ~ 1.60×10^{-4} seconds.[26] Thus the excited molecule can experience many collisions and can travel 5-10 cm before radiating. The vibrational population of the a-state may not be given by Eq. (8). However, the relative emission intensities for bands belonging to a given progression (v' constant) will still be given by Eq. (6). In Table III, we present the band-head wavelengths and relative emission intensities for the LBH system. The a-state vibrational distribution is strongly dependent on the experimental excitation conditions. When the system is excited by monoenergetic electrons (E_e > 100 eV) at low pressure (< 10^{-4} torr), the vibrational populations follow the weighting factors $q_{ov'}/A_{v'}$.[8] Under these conditions the relative emission intensities (normalized to the 3,0 band) are obtained by multiplying the tabulated values by the appropriate weighting factor. By contrast, in another experiment, the Lewis-Rayleigh afterglow of N_2 produced $N_2(a^1\pi_g)$ with v'= 0,1,2,3 highly populated but v'=4,5 only weakly so[10]. In practice, the user must exercise caution when analyzing the observed spectrum in order to account correctly for the effects of band overlap. A wavelength resolution of 1Å or better is highly recommended.

$CO(A^1\Pi - X^1\Sigma^+)$

The fourth positive group of CO consists of single headed compact bands (1400 - 2200 Å) that are degraded toward the red. The bands are readily excited by electron impact[9,33,34] in CO due to the large electronic oscillator strength for this transition[9,35] (absorption f-value = 0.19). Cascade into the A state has been shown to be negligible (< 1.5%) for moderately high electron energies[33,36] (> 100 eV). The equilibrium vibrational distribution of the A state is thus given by Eq. 8. There is at least one reference (e.g. Ref. 37) in the early literature that reports that the electronic transition moment, R_e, is constant for this system. This early work suffered from inadequate intensity calibration procedures, which led to incorrect conclusions. In fact, R_e varies quite strongly with the r-centroid. Mumma *et al.*[9] have determined the dependence of R_e on $\bar{r}$ using an optical system that was calibrated with the molecular branching ratio method (N_2 LBH system) and the atomic branching ratio method (NI multiplets). They found

$$R_e \propto 1.0 - 0.6\,\bar{r}_{v'v''}. \qquad (10)$$

No information regarding the coefficient of the second order term could be obtained because the data were adequately fitted by a straight line. This dependence was independently confirmed by the electron-energy-loss spectra of Lassettre et al.[35] who found exactly the same functional form for R_e. Because Lassettre's experiment did not use optical techniques the exact agreement constituted a direct and independent confirmation of the optical calibration techniques developed by Mumma and Zipf[8]. It also provided indirect confirmation of the constancy of R_e for the N_2 LBH system. Recent lifetime data of Imhof and Read[37] indicate that an inclusion of the quadratic term may be necessary to reproduce the observed small variation of lifetime with v'. However, the quadratic term is expected to have only a small effect on the calculated intensities for bands with r-centroids in the range $1.05 < \bar{r} < 1.35$, because R_e is well represented by Eq. 12 in that range. These bands lie to the left of the dashed line in Table IV.

The absolute transition probabilities have been calculated using the Franck-Condon factors and r-centroids of Albritton _et_ _al_.[20] and the expression for $R_e(\bar{r})$(Eq. (10)). The relative intensities were then calculated using Eq. (9) and were normalized to the (2,0) band.[9] The results are given in Table IV along with the band-head wavelengths. The lifetimes of the levels v' are typically[36,38] ~ 10 nsec, thus the limits of the emitting region correspond to the electron beam limits. For monoenergetic electron impact (> 100 eV) Table IV gives the relative volume emission rates directly. When the vibrational distribution can not be described by Eq. (8), the relative volume emission rates of bands belonging to different progressions cannot be described by Table IV. However, the relative intensities of bands within a given progression (v' constant) will still be given by the appropriate row in Table IV.

$NO(A^2\Sigma^+ - X^2\pi_r)$

The NO(A-X) γ band system occurs in the wavelength range 1900 - 3400Å. The emission bands form four heads (doublet - double headed) and are degraded to the violet. The system has been studied extensively both theoretically[20,39,40] and experimentally.[11,41,42] Franck-Condon factors and r-centroids have been calculated assuming both Morse[39] and RKR[20,40] potential functions. The recent RKR calculation of Albritton et al.[20] yields Franck-Condon factors that are in close agreement with the calculation of Nicholls,[39] which was based on Morse potential functions. The calculations of Flinn et al.[40] do not give correct relative intensities for the bands in emission, which was first noted by Callear et al.[41] and confirmed by Poland and Broida.[11] The first quantitative study of these bands in emission was performed by Robinson and Nicholls.[42] They concluded that R_e varied strongly but this was later shown to be incorrect by several authors.[11,41] Callear's comparison of the observed emission intensities with Flinn's Franck-Condon factors should be disregarded because Flinn's Franck-Condon factors have been superceded by Albritton's. However, Callear also compared the observed emission intensities with Nicholls's Morse Franck-Condon factors, which we have already noted are in good agreement with Albritton's. This comparison showed that R_e was nearly constant for $1.00 < \bar{r} < 1.10\text{Å}$. Poland and Broida showed that R_e was constant to within 10% over the band system. We have therefore taken Albritton's intensity factors and wavelengths as representative of the relative emission intensities of these bands (Table V). They may be used for calibration purposes in the range 2100-2600Å.

Poland and Broida excited the NO γ system by absorption of the Xe continuum, which resulted in extensive fluorescence (v'=0,1,2,3). They also used level-crossing spectroscopy to excite specific K' levels in the $A^2\Sigma^+$ state.[11,43] Cd^+ 2144Å radiation[11] was used to excite v'=1, K'=13 (two spin levels were excited) and the Zn 2138.56Å resonance line[43] was used to excite v'=1, K'=23 and 29. The resultant A-X rotational line radiation (1,v") was found to be highly polarized, unlike the radiation when the extended band system was excited. Considerable caution must be exercised in using the line fluorescence of NO to avoid polarization dependent effects in the measured monochromator spectral response. The extended band emission (excited by Xe continuum absorption) showed no polarization (< 2%).

The measured lifetimes of the $A^2\Sigma^+$ levels are approximately independent of v', but the levels are fed by cascade as well as excited directly.[44] The reported lifetimes[36,44] range from 200 ns to 100 ns.

$NO^+(A^1\Pi - X^1\Sigma^+)$

The $NO^+(A^1\Pi)$ state is readily excited by electron impact ionization and photo-ionization of NO. Several groups[13,14,45] have recently investigated the emission intensities of the NO^+(A-X) bands that were excited by monoenergetic electron impact. Aarts and de Heer[14] and Stone and Zipf[13] found that R_e varies to second order in $\bar{r}$ whereas Mentall and Morgan[45] were able to fit their observed intensities assuming only first order dependence on $\bar{r}$. All three groups used photo-electric detection and established their relative intensity calibrations by using the molecular branching ratio method for N_2. However, Stone and Zipf calibrated their system using the HD(B-X) line fluorescence method as well. In addition, they used the computer-least-squares-fit method in establishing their calibration curve. Finally, photoelectron spectroscopy[46] yields relative level cross sections, $\sigma_{v'}/\sigma_{o}$, and a variation of R_e with $\bar{r}$ for the $NO(X^2\pi) \rightarrow NO^+(A^1\pi)$ transition which agree well with Stone's results. For these reasons, we accept Stone and Zipf's (equivalently, Aarts and de Heer's) functional form for $R_e(\bar{r})$ for the $NO^+(A-X)$ bands and their values for the level cross sections, $\sigma_{v'}$. The relative emission intensities were calculated with Eq. (9). They are given in Table VI and apply for electron energies in excess of 100 eV.

In practice, the $NO^+(A-X)$ system is simple to use for calibration purposes because the problem of overlapping bands is not nearly so severe, as with N_2(LBH) or CO4+. However, the wavelength range (1300-1600Å) is somewhat limited.

ESTABLISHMENT OF A QUANTITATIVE CALIBRATION

The relative spectral response of an optical system may be established over a wide wavelength range by intensity measurements on the band systems mentioned. The spectral response may be made quantitative by determining the absolute detection efficiency at one wavelength, corresponding to establishing a value for G in Eq. 2.

At sufficiently high impact energies, the excitation cross section, $\sigma_{v'}$, in the Bethe approximation is given by[47]

$$\sigma_{v'} = \frac{4\Pi a_o^2 R^2}{E_{el}} \frac{f_{ov'}}{E_{ov'}} \ln(4CE_{el}/R), \tag{11}$$

where a_o is the first Bohr radius, R is the Rydberg energy, $E_{ov'}$ is the excitation energy, C is a constant, and E_{el} is the energy of the incident electron. In the absence of cascade into level v', quenching, or excitation transfer, the emission cross section of the (v',v") band is given by

$$\sigma_{v'v''} = \frac{A_{v'v''}}{A_{v'}} \sigma_{v'}, \tag{12}$$

and thus depends on R_e through Eq. (3). Aarts and de Heer[33] established that the $CO(A^1\pi)$ state was not populated by cascade and they used Eqs. (11) and (12), along with preliminary f values of Lassettre and Skerbele (final f values were ~ 10% higher, see Ref. 35) to establish quantitative cross sections for the (0,1) band of $CO(A^1\pi - X^1\Sigma^+)$. However, they assumed constant R_e, which was later shown to vary quite strongly with $\bar{r}$ by Mumma et al.[9] thus affecting the cross section $\sigma_{v'v''}$ through the branching ratio in Eq. (12). Using the correct branching ratio and the published f values[35], we have recalculated the emission cross section at 500 eV (Bethe theory). The value of the constant C in Eq. (11) may be determined for each v' from the coefficients in the expansion for the generalized oscillator strength[48],

$$f(k) = \frac{f_o}{(1 + X)^6} \left\{ 1 + \sum_{m=1}^{\infty} \frac{f_m}{f_o} \left(\frac{X}{1 + X} \right)^m \right\} , \tag{13}$$

where K is the momentum transferred by the impacting electron, $X = (Ka_o)^2/\alpha^2$, and $\alpha = \sqrt{Q/R} + \sqrt{(Q-E_{v'})/R}$. Q is the ionization potential of the orbital being excited. Then,

$$\ell n\ C = 2\ell n\ (\alpha\ R/E_{ov'}) - \frac{137}{60} + \frac{f_1}{6f_o} + \frac{f_2}{42f_o} + \cdots \tag{14}$$

The generalized oscillator strength has been accurately measured by Lassettre and Skerbele and they find[49] $f_o = 0.0427$, $f_1 = 0.0893$, and $f_2 = 0.0165$ for excitation of $v' = 2$. Using these data, we find $\ell n\ C = 0.0514$ ($v' = 2$) and $\ell n\ C = 0.1635$ ($v' = 0$). Combining these values with Eq. (11) and the branching ratios of Mumma et al., we find

$$\sigma_{0,1}\ (500\ \text{eV}) = 5.4 \times 10^{-19}\ \text{cm}^2 \pm 7\%, \tag{15}$$

and

$$\sigma_{2,2}\ (500\ \text{eV}) = 4.4 \times 10^{-19}\ \text{cm}^2 \pm 7\%. \tag{16}$$

The error estimate includes estimated rms errors of 5.5% in Lassettre and Skerbele's f-values and 3% in the branching ratios. The total rms error is thus ± 6.3% which we round upward to 7%. This rms error (7%) is thought to be realistic. These values for $\sigma_{0,1}$ and $\sigma_{2,2}$ may be used to establish a quantitative spectral response at 1597Å and

1577Å respectively.

The principle of using the absorption oscillator strength and the Bethe theory to establish quantitative cross sections has recently been applied in the extreme vacuum ultraviolet as well by van Raan (λ < 1164Å) using noble gas resonance lines.[50]

The quantitative response may also be established by measurements of the emission intensity of Lyman alpha radiation, HI 1216Å, produced by electron impact dissociative excitation[49] of H_2. This cross section has been placed on an absolute scale by comparison with the cross section for exciting Lyman alpha by electron impact on atomic hydrogen, which was normalized to the Born approximation above 300 eV. At 100 eV, the value of the dissociative excitation cross section is

$$\sigma(1216) = 1.2\text{x}10^{-17} \text{ cm}^2 \pm 11\%. \qquad (17)$$

The error reflects the fact that the dissociative excitation cross section is related to the theoretical value of the direct excitation cross section by experiment. A wavelength resolution of ~ 1Å is required to separate the Lyman alpha line from neighboring lines of the H_2(C-X) Werner bands.

DISCUSSION

We indicate the internal consistency of this calibration technique by noting that Mumma et al.[9] established a quantitative spectral response for their optical system through measurements on Lyman alpha[51] (1216Å), using Eq. (17), and the relative intensities of the N_2 LBH system and certain NI multiplets.[8] They then measured the emission cross section for the CO fourth positive bands at 1597Å, consisting of the (0,1) band (95%) and the (6,5) band (5%). Their measured cross section extrapolates to 5.8×10^{-19} cm^2 $\pm$ 13% at 500 eV. Thus, their cross section for the (0,1) band is 5.5×10^{-19} cm^2 $\pm$ 13% at 500 eV, which is in agreement with Eq. (15). The close agreement suggests that the error bars are realistic, and perhaps even conservative.

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TABLE I. Wavelengths and Transition Probabilities of H_2 and HD ($B^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$) Lines.

	H_2				HD			
Band	Line	λ (Å)	$A_{\nu'J'\nu''J''}$ ($\times 10^8$ s^{-1})	Relative Intensity	Line	λ (Å)	$A_{\nu'J'\nu''J''}$ ($\times 10^8$ s^{-1})	Relative Intensity
3,0	R(0)	1062.8	0.336	0.141	R(1)	1066.7	0.256	0.131
	P(2)	1066.8	0.705	0.296	P(3)	1071.8	0.411	0.210
3,1	R(0)	1112.0	0.759	0.319	R(1)	1109.7	0.792	0.405
	P(2)	1116.2	1.518	0.637	P(3)	1114.9	1.215	0.622
3,2	R(0)	1162.7	0.305	0.128	R(1)	1153.9	0.652	0.334
	P(2)	1167.1	0.555	0.233	P(3)	1159.3	0.924	0.473
3,3	R(0)	1214.9	0.046	0.019	R(1)	1199.2	0.028	0.014
	P(2)	1219.4	0.125	0.052	P(3)	1204.8	0.021	0.011
3,4	R(0)	1268.4	0.546	0.229	R(1)	1245.6	0.333	0.170
	P(2)	1273.0	1.110	0.466	P(3)	1251.4	0.565	0.289
3,5	R(0)	1322.8	0.232	0.097	R(1)	1292.9	0.615	0.315
	P(2)	1327.5	0.401	0.168	P(3)	1298.8	0.884	0.453
3,6	R(0)	1377.7	0.093	0.039	R(1)	1340.8	0.062	0.032
	P(2)	1382.5	0.240	0.100	P(3)	1346.8	0.053	0.027
3,7	R(0)	1432.6	0.600	0.251	R(1)	1389.2	0.293	0.150
	P(2)	1437.4	1.205	0.506	P(3)	1395.2	0.521	0.267
3,8	R(0)	1486.8	0.132	0.055	R(1)	1437.5	0.670	0.343
	P(2)	1491.6	0.196	0.082	P(3)	1443.6	0.966	0.495
3,9	R(0)	1539.3	0.325	0.136	R(1)	1485.4	0.075	0.038
	P(2)	1543.9	0.779	0.327	P(3)	1491.5	0.059	0.030
3,10	R(0)	1588.6	1.187	0.498	R(1)	1532.2	0.407	0.208
	P(2)	1593.3	2.382	1.000	P(3)	1538.2	0.754	0.386
3,11	R(0)	1634.0	0.542	0.227	R(1)	1577.2	1.284	0.658
	P(2)	1638.0	0.955	0.400	P(3)	1583.0	1.952	1.000
3,12	R(0)	1672.7	0.0071	0.0029	R(1)	1619.5	0.768	0.393
	P(2)	1676.1	0.0054	0.0022	P(3)	1625.0	1.018	0.521
3,13	R(0)	1702.6	0.0054	0.0022	R(1)	1657.9	0.076	0.039
	P(2)	1705.2	0.0131	0.0054	P(3)	1662.9	0.075	0.038

c

TABLE II. Wavelengths and Relative Intensities for Q1 Lines of the

$H_2(C^1\Pi_u - X^1\Sigma_g^+)$ Werner Band System

	v''=0	1	2	3	4	5	6	7	8	9	10	11	12	13
v'														
0	319 1009.9*	809 1054.1	974 1099.5	386 1146.0	98 1193.3	12 1241.2								
1	780 986.9	551 1029.1	13 1072.3	759 1116.5	1000 1161.3	437 1206.7	76 1252.1	4 1297.2						
2	745 966.2	49 1006.6	411 1047.9	270 1090.0	126 1132.8	905 1175.9	711 1219.0	168 1261.7	10 1303.4					
3	475 947.5	21 986.3	307 1026.0	10 1066.3	358 1107.2	11 1148.3	463 1189.4	728 1230.0	227 1269.6	12 1307.6				
4	245 930.6	86 968.1	84 1006.2	119 1045.0	61 1084.2	142 1123.6	105 1162.9	151 1201.7	580 1239.5	231 1275.7	8 1309.4			
5	114 915.7	93 951.9	6 988.8	102 1026.3	2 1064.0	101 1101.9	15 1139.7	125 1177.0	30 1213.5	413 1249.0	193 1282.9	2 1315.0	1 1344.8	
6	50 902.2	67 937.3	2 273.1	43 1009.3	27 1045.8	16 1082.4	54 1118.8	2 1154.8	82 1189.9	3 1224.0	289 1256.6	134 1287.3		
7	21 890.1	40 924.3	8 959.1	11 994.3	28 1029.7	1069.1	28 1100.4	12 1135.1	14 1169.0	39 1201.9	1233.3	214 1262.9	68 1290.3	8 1315.3

* Wavelengths after E. J. Stone, private communication.

TABLE III. Wavelengths and Relative Emission Intensities for the $N_2(a^1\Pi_g - X^1\Sigma_g^+)$ Lyman-Birge-Hopfield System.

v'	v''=0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
0	215 1450	683 1501	1000 1555	896 1612	552 1672	247 1736	83 1805	21 1878	4 1956										
1	665 1416	1000 1464	371 1515	2 1570	337 1627	624 1688	518 1752	266 1821	95 1895	24 1973	5 2057								
2	1000 1384	513 1430	16 1479	463 1530	325 1585	2 1642	211 1703	458 1768	389 1838	195 1911	65 1990	16 2074	3 2165						
3	1000 1354	61 1398	338 1444	275 1493	15 1545	313 1600	183 1658	1 1719	196 1785	340 1854	254 1928	114 2007	34 2092	8 2182					
4	1000 1325	35 1368	493 1412	2 1459	325 1508	133 1560	64 1616	293 1674	88 1736	30 1801	246 1871	310 1945	189 2025	72 2109	19 2200	4 2297			
5	1000 1299	348 1339	315 1382	210 1427	308 1474	47 1523	353 1576	25 1631	184 1690	268 1752	14 1818	119 1888	333 1963	296 2042	143 2127	47 2218	10 2315	1 2420	
6	1000 1273	926 1312	45 1353	654 1396	20 1441	470 1489	88 1539	257 1592	282 1648	17 1707	352 1769	178 1835	14 1906	298 1981	430 2060	276 2145	106 2236	26 2333	4 2438

TABLE IV. Bandhead Wavelengths and Relative Emission Intensities of the CO($A^1\Pi$-$X^1\Sigma^+$) Fourth Positive Group.

v'	v''=0	1	2	3	4	5	6	7	8	9	10	11	12
0	147 1544.5	268 1597.4	230 1653.3	123 1712.4	46 1775.2	12 1841.8	2 1912.7						
1	703 1509.9	391 1560.4	5 1613.7	127 1670.0	240 1729.6	174 1792.8	74 1859.9	22 1931.2					
2	1000 1477.6	33 1525.9	261 1576.9	246 1630.6	6 1687.4	84 1747.5	171 1811.2	123 1878.7	52 1950.5	15 2027.	3 2108.5		
3	744 1447.4	87 1493.7	308 1542.5	0 1593.9	162 1648.1	104 1705.4	0 1766	61 1830.2	95 1898.2	61 1970.6	23 2047.5	6 2129.6	
4	375 1419.1	258 1463.6	59 1510.4	113 1559.7	82 1611.5	12 1666.3	87 1724.1	28 1785.2	3 1849.9	37 1918.5	42 1991.4	23 2068.9	8 2151.5
5	143 1392.6	237 1435.4	3 1480.4	108 1527.7	0 1577.4	66 1629.8	9 1685.05	20 1743.4	34 1805.0	4 1870.3	5 1939.5	18 2013	15 2091.1
6	44 1367.6	131 1408.9	40 1452.3	25 1497.7	32 1545.5	16 1595.8	12 1648.7	21 1704.5	0 1763.4	13 1825.6	9 1891.5	0 1961.3	4 2035.4
7	12 1344.2	54 1384.1	45 1425.9	0 1469.7	26 1515.7	0 1564	16 1614.8	0 1668.3	10 1724.6	3 1784.1	2 1847	5 1913.5	1 1983.9

TABLE V. Wavelengths and Relative Emission Intensities of the $NO(A^2\Sigma^+ - X^2\Pi)$ γ Band System.

	v''=0	1	2	3	4	5	6	7
v'								
0	721 2265.5	1000 2366.0	786 2474.2	463 2590.9	228 2717.0	100 2853.8	40 3002.5	15 3164.8
1	1000 2151.3	274 2241.8	--- 2338.7	147 2442.7	238 2554.4	206 2675.0	132 2805.2	71 2946.4
2	1000 2049.5	53 2131.5	420 2218.8	173 2312.2	--- 2412.1	63 2519.4	141 2634.5	145 2758.7
3	820 1958.1	1000 2032.8	193 2112.2	163 2196.6	393 2286.6	150 2382.7	--- 2485.5	56 2595.7

TABLE VI. Bandhead Wavelengths and Relative Intensities of the $NO^+(A^1\Pi - X^1\Sigma^+)$ Baer-Mischer Band System.

v'	v''=0	1	2	3	4	5
0	192 1368.3	641 1413.7	1000 1461.4	983 1511.8	676 1564.9	349 1621.1
1	256 1339.7	466 1383.1	281 1428.8	29 1476.9	33 1527.6	145 1581.0
2	150 1313.0	127 1354.7	8 1398.5	26 1444.6	51 1493.0	15 1544.0
3	52 1288.2	15 1328.3	3 1370.4	14 1414.5	2 1461.0	3 1509.8