NATIONAL BUREAU OF STANDARDS REPORT

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A CURVE OF GROWTH DETERMINATION OF THE F-VALUES FOR THE FOURTH POSITIVE SYSTEM OF CO AND THE LYMAN-BIRGE-HOPFIELD SYSTEM OF N_2

Technical Report
to
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U.S. DEPARTMENT OF COMMERCE

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A Curve of Growth Determination of the f-values for the Fourth Positive System of CO and the Lyman-Birge-Hopfield System of N_2

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Abstract

The curve of growth method has been employed to determine f-values for the fourth positive system of CO and the magnetic dipole and electric quadrupole components of the Lyman-Birge-Hopfield system of N_2. The transition moments are, respectively, 0.83 a_oe, 5.9 x 10^{-11} Bohr magnetons and 2.6 a_o^2e. No significant dependence on r-centroid was found. The mean value of the ratio of the electric quadrupole to magnetic dipole f-values was 0.076.

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Introduction

Current interest in elementary processes involving electronically excited diatomic molecules demands an accurate knowledge of radiative lifetimes and oscillator strengths. Several methods are available for their determination. These include direct measurement of the lifetime by the phase shift technique[1], and measurement of the integrated absorption coefficient by optical absorption spectroscopy.[2,3] The latter method is severely limited by resolution requirements. In some instances this has been overcome by the use of very high pressures to broaden the rotational fine structure.[4] Alternatively, if spectrographs of sufficiently high resolving power are available, the curve of growth method may be employed.[2,3] Recently, Lassettre and coworkers[5] have exploited the technique of electron impact spectroscopy. Here there is no need to resolve the individual rotational lines, but the general applicability of the method has not been thoroughly tested. This can only be achieved comparing f-numbers derived from electron impact work with those obtained by other methods.

In the present work, the f-numbers for three electronic transitions, the fourth positive system of CO, and the magnetic dipole and electric quadrupole components of the Lyman-Birge-Hopfield system of N_2, are determined by the curve of growth method. The equations used for the averaging of f-numbers, A-values and lifetimes are clearly defined so that the numbers

derived here can be properly compared with independent determinations by other methods where slightly different averaging procedures were employed.

Theory

If a parallel beam of light, intensity I_o, is incident on a cell, ℓ cm long, containing a monatomic gas of density N atoms per cc, then the light transmitted at frequency ν (cm^{-1}) is given by[2,3]

$$I_\nu = I_o \exp\left(-\sigma(\nu)\right)N$$

where $\sigma(\nu)$ is the absorption cross section (cm^2). The equivalent width, $W(cm^{-1})$, for an isolated spectral line is defined as $W = \int_{-\infty}^{\infty} [1-\exp(-\sigma(\nu)N\ell)]d\nu$. The relationship between W and the oscillator strength f is complex, and is dependent on the ratio of the collision broadened plus natural line width to the Doppler line width (a). Curves of growth are plots of $\log_{10}(W/2\delta)$ against $\log_{10}(10.6\ \sigma_o N l)$,[6] where δ is the half width at maximum over e for a Doppler line, and σ_o is the peak cross-section

$$\delta = \frac{\nu_o}{c}\left(\frac{2RT}{M}\right)^{1/2}$$

and

$$\sigma_o = \frac{1}{\delta\sqrt{\Pi}} \int \sigma(\nu)d\nu$$

$$= \frac{\sqrt{\Pi e^2 f}}{mc\ \delta} = (5 \times 10^{-13}\ f/\delta)\ cm^2$$

for δ in cm^{-1}. For $W/2\delta \lesssim 0.5$, the plots become linear, and the dependence on (a) becomes less marked. Valid extrapolation can

then be made to zero optical path length, and the f-value determined. If the resolving power of the spectrograph is sufficiently large that the observed spectral line width is not much larger than the real width, then accurate measurements can be made in the linear region.

These considerations still apply for all isolated rotational lines in the electronic spectrum of a diatomic molecule. However, the relationships between the f-number for a given line and the overall electronic transition moment, and between the number of molecules in a given lower rotational level and the overall gas density, must be considered.

For electric dipole and magnetic dipole transitions, the oscillator strength for absorption of a rotational line (J', J") of a vibronic band (n, v'; m, v") is given by[7,8]

$$f_{nv'J',mv''J''} = \frac{8\pi^2 mc\nu_{v'J',v''J''}}{3he^2} \frac{\left|R_e^{nv'J',mv''J''}\right|^2}{(2J''+1)\ (2-\delta_{o,\Lambda''}\ (2S''+1))} \quad (1)$$

where $\delta_{o,\Lambda''}$ is the Kronecker delts, and all other symbols have their usual meanings.

Assuming no interaction between rotational, vibrational and electronic motions.

$$|R_e^{nv'J',mv''J''}|^2 = S_{J'J''}q_{v'v''}|R_e^{nm}\cdot(\bar{r}_{v'v''})|^2 \quad (2)$$

where $S_{J'J''}$ is the rotational line strength, $q_{v'v''}$ is the Franck-Condon factor and $|R_e^{nm}(\bar{r}_{v'v''})|$ is the electronic transition moment, which may be dependent on the r-centroid $\bar{r}_{v'v''}$.[9]

The following summations apply:

$$\sum_{J''} S_{J'J''} = 2J' + 1, \quad \sum_{J'} S_{J'J''} = 2J'' + 1 \tag{3}$$

$$\sum_{v'} q_{v'v''} = \sum_{v''} q_{v'v''} = 1 \tag{4}$$

Thus,

$$f_{nv',mv''} = \sum_{J'} f_{nv'J',mv''J''} = \frac{8\pi^2 mc\nu_{v'v''}}{3he^2} \cdot \frac{|R_e^{nm}|^2 \cdot q_{v'v''}}{(2-\delta_{0,\Lambda''})(2S''+1)} \tag{5}$$

For electric quadrupole transitions

$$f_{nv'J',mv''J''} = \frac{4\pi^4 mc\nu^3_{v'J',v''J''}}{5he^2} \; \frac{|R_e^{nv'J',mv''J''}|^2}{(2J''+1)(2-\delta_{0,\Lambda''})(2S''+1)} \tag{6}$$

The Einstein transition probability for spontaneous emission is given by

$$A_{nv'J',mv''J''} = \frac{64\pi^4\nu^3_{v'J',v''J''}}{3h} \; \frac{|R_e^{nv'J',mv''J''}|^2}{(2J'+1)(2-\delta_{0,\Lambda'})(2S'+1)} \tag{7}$$

for an electric or magnetic dipole transition; and by

$$A_{nv'J',mv''J''} = \frac{32\pi^6\nu_{v'J',v''J''}}{5h} \; \frac{|R_e^{nv'J',mv''J''}|^2}{(2J'+1)(2-\delta_{0,\Lambda'})(2S'+1)} \tag{8}$$

for an electric quadrupole transition.

Thus, for CO, the J independent lifetime of a given excited vibronic state is given by

$$\tau^{-1}_{nv'} = \sum_{v''} A_{nv',mv''} = \frac{64\pi^4}{3hw_n} \cdot \sum_{v''} \left(|R_e^{nm}|^2 \; q_{v'v''}\nu^3_{v'v''}\right) \tag{9}$$

neglecting the small variation in frequency of the rotational lines over a vibronic band. For the fourth positive system of CO, the degeneracy

$$w_n = (2-\delta_{o,\Lambda'})(2S'+1) = 2$$

For the Lyman-Birge-Hopfield system of N_2,

$$\tau^{-1}_{nv'} = \frac{64\Pi^4}{3hw_n} \cdot \sum_{v''} \left(|R_e^{nm}|^2_D q_{v'v''} \nu^3_{v'v''}\right) + \frac{32\Pi^6}{5hw_n} \sum_{v''} \left(|R_e^{nm}|^2_Q q_{v'v''} \nu^5_{v'v''}\right) \qquad (10)$$

where $|R_e^{nm}|_D$ and $|R_e^{nm}|_Q$ are the magnetic dipole and electric quadrupole transition moments respectively, and $w_n = 2$.

For a heteronuclear molecule with a $^1\Sigma^+$ ground state, the number density of molecules in the J" level is

$$N_{J''} = \frac{N(2J''+1)\ \exp[-hB''cJ''(J''+1)/kT]}{f} \qquad (11)$$

where $f = kT/hB''c$. N is the total number of molecules and $N_{J''}$ is the number in a given rotational level, all other symbols have their usual meanings.

For nitrogen,

$$N_{J''} = \sum_T N\ \frac{(2T+1)(2J''+1)\exp(-hB''cJ''(J''+1)/kT)}{f}$$

In eq. (12), $f = \sum_{T=0}^{2} (2T+1)kT/2hB''c$.

For even J", the total nuclear spin quantum number T can take the values 2 and 0, while for odd J" it can take the value 1. In evaluating f, the summation is taken over all three values of T.

The rotational line strengths for the electric and magnetic dipole transitions were derived by Hönl and London,[10] and have been tabulated by Herzberg.[7] For the electric quadrupole transition they are given by Chiu.[9] Nicholls'[12] Morse Franck-Condon factors were used for CO, and Benesch[13] et al's

RKR Franck-Condon factors for N_2. Nicholls[12] (Morse) and Zare et al[14] (RKR) have also calculated Franck-Condon factors for N_2. The differences among the three arrays are insignificant ($\lesssim$ 2%) over the range of interest.

Experimental

Spectra were photographed on Kodak SWR plates, using a 6m Eagle spectrograph in the fourth order. The background was provided by a krypton discharge lamp, powered by a 2450 Mc/S power supply, with spectrograph slits of 3×10^{-2} and 9×10^{-2} cm. Several background intensities were used, and each plate was calibrated for density vs. intensity. The absorption cell was 2 cm long, and was fitted with LiF windows. Pressures less than 500 Nm^{-2} were measured with a calibrated capacitance micromanometer, while a precision dial gauge was used for higher pressures. Ultra high purity gases were employed without further purification.

Results

$\mathrm{Log}_{10}\,(W/2\delta)$ was plotted against $\log_{10} N_{J''}S_{J'J''}/(2J''+1)$, and extrapolated to $(W/2\delta) = 0.1$ to give $(N_{J''}S_{J'J''}/(2J''+1))_{0.1}$. At this point, $10.6\,\sigma_o N_{J''} l = 1.28$;

thus $f_{nv',mv''} = \dfrac{1.28mc\delta}{10.6\, e^2 \ell\sqrt{\pi}} \left\{ \dfrac{2J''+1}{N_{J''}S_{J'J''}} \right\}_{0.1}$.

Figs. 1-3 show plots for CO($A^1\Pi(v=4) \leftarrow X^1\Sigma^+(v=0)$) and for the (0,0) and (5,0) magnetic dipole components and the (2,0) and (3,0) electric quadrupole components of the Lyman-Birge-Hopfield system of N_2.

Experiments were conducted at three pressures for both gases, and extrapolations made over the linear range by a least squares fit. Over this range, there is little dependence on pressure broadening, and a single composite graph was used for all three pressures.

Wherever possible the data were extended beyond the linear region. Some difficulties were, however, encountered in this respect. With an observed line width of ~ 0.4 cm^{-1}, the apparent integrated absorption dropped below the theoretical value as $(\Delta I/I_o)$ at the peak of the absorption line became progressively greater than ~ 0.4 (in the case of CO, the apparent integrated absorptions dropped significantly below the Doppler curve). On increasing the slit width by a factor of 3, and thereby reducing (I/I_o) max, the apparent integrated absorption increased to its theoretical value. Oldenburg and Rieke[15] report similar observations. We believe the explanation for this phenomenon lies in the finite grain size of the emulsion. At higher densities and smallest slit settings the grains are of size comparable to the line width. At low density the grains are smaller. Therefore two slit widths were used throughout this investigation, the

narrow slit being used for low intensity lines, and the wide slit for higher intensity lines. The two were found to link satisfactorily with one another.

The CO measurements were made at low pressures (<133 Nm^{-2}), and the curves of growth were Doppler. For N_2, however, much higher pressures were used, which enabled an estimate of $(6 \pm 3) \times 10^{-15}$ cm^2 to be made for the pressure broadening cross-section. This is somewhat less than the value derived by Shemansky[16] $((1.6 \pm 0.5) \times 10^{-14}$ $cm^2)$. The gas kinetic cross-section is 1.1×10^{-15} cm^2.

No f-values were obtained for the $N_2(4,0)$ band because of chance overlap of the rotational lines in the region most suitable for accurate measurements at the optical path lengths used in this work.

Discussion

The absolute values for $|R_e^{nm}|$ for the three transitions studied are shown in Tables 1-3. No significant variation of the electronic transition moment was found. Tables 5, 6 also show the values obtained for $|R_e^{nm}|$ by other methods. For the fourth positive system of CO, the most extensive previous investigations were by Hesser[17], Rich[18], and Meyer et al.[19] Hesser[17] measured the radiative lifetimes by the phase-shift technique. Rich[18] looked at absorption in shock-heated carbon monoxide, and in addition to the two (v"=0) bands, he measured the f-values for several bands in the (v"=1-3) progressions.

He found a mean value for $|R_e^{nm}|$ of 0.76 ± 0.10 au. Meyer et al,[19] studied the electron impact spectrum. This involves measuring the generalized oscillator strength as a function of the momentum change of the electrons, and extrapolating to zero momentum change to give the optical oscillator strength. The data shown in Table 5 were obtained several years ago, and show some dependence on upper state vibrational quantum number. Since then the apparatus has been refined, and the resolution increased, and the latest relative values show extremely good agreement with Franck-Condon factors.[20] However, the dependence on momentum change has not been investigated. The only other measurements which have been made were by Hexter[21] and Brith and Schnepp,[22] who calculated the f_{ee} values from Davydov splittings in the solids. They obtained respectively 0.148 for v'=2 and 0.16 for v'=0-3.

The Lyman-Birge-Hopfield system of nitrogen has been extensively investigated. Lichten[23] and Olmsted et al.[24] measured the radiative lifetime of $N_2a^1\Pi_g$ by means of a molecular beam technique, using excitation by electron bombardment. They found $\tau = 1.7 \times 10^{-4}$ sec and $(1.2 \pm 0.5) \times 10^{-4}$ sec respectively. These are equivalent to f_{ee} values of 5×10^{-6} and 7×10^{-6}. Holland[25] looked at the profile of emission following excitation by a beam of electrons, and found that it was consistent with a lifetime $< 8 \times 10^{-5}$ sec ($f_{ee} > 10^{-5}$). Jeunehomme,[26] investigating the emission from a pulsed discharge, found a strong pressure dependence in the lifetime of $N_2a^1\Pi_g$, and deduced a radiative lifetime of $(5\text{-}10) \times 10^{-6}$ sec, corresponding

to $f_{ee} \simeq 10^{-5}$.

Ching, Cook, and Becker[27] measured the oscillator strengths for the Lyman-Birge-Hopfield system using pressures of up to 40 atm. to broaden the rotational fine structure, and thus make the system amenable to low resolution absorption study. The $|R_e^{nm}|_D$ values deduced from their results are shown in Table 6. The data are corrected for the contribution arising from the electric quadrupole component of the transition, using the values of $(f_{ee})a/(f_{ee})D$ shown in Table 4. The values are considerably larger than our own, and correspond to overall radiative lifetimes of $(2.7 - 4.1) \times 10^{-5}$ sec. Ching et al. found a residual weak dependence of the absorption coefficients on pressure, and they extrapolated this to zero pressure to obtain the f-values. Recently, Shemansky[16] has shown that this variation in an artifact, but applying his correction leads to even larger values for $|R_e^{nm}|_D$.

Shemansky[16] evaluated the f-numbers by fitting theoretical and experimental curves of growth and band profiles, obtained with a low resolution spectrograph. The values of $|R_e^{nm}|_D$ he obtained are shown in Table 6. They correspond to lifetimes rising from 1.4×10^{-4} sec for $v = 0$ to 1.6×10^{-4} sec for $v = 6$, with a probable error of ∿20%. He also derived a self-broadening cross section of 1.6×10^{-14} cm^2, which is again larger than our own.

The electric quadrupole component of the Lyman-Birge-Hopfield system was first investigated by Wilkinson and Mulliken.[28,29] Using James and Coolidge's[30] line strengths for $a^1\Sigma_g^+ - {}^1\Sigma_g^+$ transition, they obtained a value of 0.15 for $(f_{ee})_Q/(f_{ee})_D$. Following Chiu's[11] tabulation of line strengths for a $^1\Pi g$ - $^1\Sigma_g^+$ transition, Vanderslice et al.[31] reinvestigated the high resolution spectrum of nitrogen, and derived $(f_{ee})_Q/(f_{ee})_D = 0.33$. Their method was approximate, since they did not use a curve of growth technique. Thus they compared directly two sets of absorption lines, which differed substantially in intensity. Clearly, such a method tends to over-estimate the relative f-value of the weaker component. Furthermore, they did not apply the normalization procedure used here (see Appendix and equation) with Tables 3,4. This corresponds to $|R_e^{nm}|_Q^2/|R_e^{nm}|_D^2 = 1.3 \times 10^{-11}$.

Shemansky[16] compared the profiles of the magnetic dipole and electric quadrupole components under Doppler conditions, and found $(f_{ee})_Q/(f_{ee})_D$ values ranging from 0.08-0.10. These correspond to $|R_e^{nm}|_Q^2/|R_e^{nm}|_D^2 = 5.6 \times 10^{-12}$, and are in good agreement with our values. Once again, his ratio has been redefined so as to be consistent with the ratio used here.

Garstang[32] analysed Lassettre and Krasnow's[33] electron energy loss results for the Lyman-Birge-Hopfield system, and derived a radiative lifetime for the quadrupole transition of 5×10^{-4} sec., which is about four times shorter than the lifetimes shown in Table 3. However, this value is based on some

of Lassettre's earlier work in which the vibrational structure was completely unresolved.

The f-values determined here are, with the exception of those for the electric quadrupole transition, based on measurements of the P, Q, and R branches for relatively high J" values (J"=8-30). (For the quadrupole transition, low rotational levels of the S branch were used.) This raises the question of the relevance of Franck-Condon factors calculated for rotationless potential curves in applications of this sort. Learner[34] examined the influence of vibration-rotation interaction on absorption intensities for OH. He found some variation, which was most marked for the weaker bands, where cancellation effects are important. He also incorporated an $\bar{r}$ dependence for $|R_e^{nm}|$, and in this case found a much larger variation of effective Franck-Condon factor with J. More recently, Villarejo et al.[35] found a large effect for the H_2 Lyman transition, for which there is a large change in r_e, but little variation for the Fulcher bands. Several transitions in nitrogen have been examined by Benesch et al.[36] and Schumaker.[37] Neither investigation revealed any significant variation of $q_{v'v''}$ with J. The Lyman-Birge-Hopfield system, however, was not studied. Any effect is likely to be most noticeable for lighter molecules, in transitions with a large change in r_e. It is, therefore, unlikely to be of much importance in the transitions studied here.

In addition, the variations found by Learner[34] and by Villarejo et al.[35] were erratic, and would lead to a large amount of scatter in the curves of growth, particularly as the pressure is changed. Any large effects can, therefore, be discounted.

Nadler and Kaskan[38] found a dependence of the collisional broadening parameter, (a), on J for OH ($A^2\Sigma^+ - X^2\Pi$). This led them to question the validity of curve of growth procedures for determining f-values. If such a phenomenon did exist for N_2 and CO, then it would not affect the f-values derived here, since the linear portion of the curve of growth was used exclusively, and there is little dependence of the equivalent width on (a) in this region.

The only other factor which could invalidate the present work is the possible occurrence of perturbations. Both systems have been extensively analysed[39,40] and perturbations tabulated, and these rotational lines were avoided. The most prominent example was the Q(23) line of the (4,0) band of CO. This line was in fact slightly weaker than the line to the perburbing level $I^1\Sigma^-(v=6, J=23)$.

Unless a very large data sample is taken, the curve of growth method is not capable of quite the same accuracy as other techniques, such as electron energy loss and phase shift measurements. However, it is the most direct method, and is

dependent only on the assumption of the separability of rotational and vibrational motions. At present there are large uncertainties and inconsistencies in published f-values. It is, therefore, important that these quantities are constantly reinvestigated by a variety of experimental techniques, until consistency is achieved.

Appendix

Two definitions of the degeneracy factors to be used in equations 1,5-10, and consequently of the absolute transition moment, have appeared in the literature. While both are internally consistent, in that experimental observables, f and A, are related via the ratio of such factors, the out-of-context use of a previously determined electronic transition moment can lead to erroneous results if employed with a different definition of degeneracy.

The convention followed here is that adopted by Herzberg.[7] Consider transitions between an initial orbital ϕ''_k, which is one of a degenerate set, and a set of final orbitals ϕ'_i. The probability of a transition from ϕ''_k to all ϕ'_i is taken as the total probability of transitions from all levels degenerate with k to all i, divided by the degeneracy of k. Thus,

$$f_{nv',mv''} = \frac{8\pi^2 mc\nu_{v'v''}}{3he^2} \frac{|R_e^{nm}|^2 q_{v'v''}}{w_m}$$

where $|R_e^{nm}|^2 = \sum_i \sum_k |R_e^{ik}|^2$

and $w_m = (2-\delta_{o,\Lambda''})(2S'' + 1)$

$A_{nv',mv''}$ is defined as in equation 9.

In Mulliken's[41] notation, equation 5 is replaced by

$$f_{nv',mv''} = \frac{8\pi^2 mc\nu_{v'v''}}{3he^2} \cdot G_n |R_e^{nm}|^2 q_{v'v''}$$

and equation 9 by

$$\sum_{v''} A_{nv',mv''} = \frac{64\pi^4 GM}{3h} \sum_{v''}(|R_e^{nm}|^2 q_{v'v''}\nu^3_{v'v''})$$

If the probability of a transition from ϕ''_k to a single orbital ϕ'_i is $|R_e^{ik}|^2$, then the total probability of a transition ϕ''_k to all ϕ'_i is $G_n|R_e^{ik}|^2$, where G_n is the total number of degenerate final orbitals with which the initial orbital can combine. $|R_e^{ik}|^2$ is taken as $|R_e^{nm}|^2$. Mulliken discusses in detail the definitions of G_n and G_m.

In the present cases, $G_n = 2$, and $w_m = 1$, and the Mulliken notation therefore leads to values of $|R_e^{nm}|^2$ which are half those derived in this paper. The Mulliken notation is used by both Hesser[17] and Shemansky.[16]

Further difficulties arise in the sum rule employed for rotational line strengths. In the present work the electronic transition moments have been directly related to the transition probabilities, i.e.

$$\sum_{v'} \sum_{J'} f_{nv'J',mv''J''} = \frac{8\pi^2 mc\nu_{v'v''}}{3\ he^2} \cdot \frac{|R_e^{nm}|^2}{w_m}$$

The Franck-Condon factors and rotational line strengths have been interpreted simply as branching ratios, i.e. the sum rules (3) and (4) have been applied.

Frequently, however, line strengths derived in the literature have not been normalised in this way. For example, Shemansky[16] and Vanderslice et al.[31] directly used Chiu's[11] line strengths for the quadrupole $^1\Pi_g - ^1\Sigma_g^+$ transition. On summation, these give $4/3(2J'' + 1)$. In addition, summation of their line strengths for the magnetic dipole transition gives $2(2J'' + 1)$. Essentially, we have absorbed the factors 4/3 and 2 into the electronic transition moment, and this accounts for the discrepancy in our definitions of $|R_e^{nm}|_Q^2/|R_e^{nm}|_D^2$.

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Figure Captions

Figure 1: Curve of growth for the (4,0) band of the CO fourth Positive System.

○ [CO] = 27 Nm^{-2} ◐ [CO] = 66 Nm^{-2} ● [CO] = 133 Nm^{-2}

Δ Q(J'=23); [CO] = 27 Nm^{-2} ▲ $I'\Sigma^-$(V=6, J=23) - $X^1\Sigma^+$ (V=0, J=23); [CO] = 27 Nm^{-2}

——— Least squares fit to points on linear portion of graph.

— — — Doppler curve for (W12δ) > 0.7

Figure 2: Curves of growth for the (0,0) and (4,0) bands of the magnetic dipole component of the Lyman-Birge-Hopfield system of nitrogen.

○ [N_2] = 2 x 10^4 Nm^{-2}; ◐ [N_2] = 4.85 x 10^2 Nm^{-2}; ● [N_2] = 10^5 Nm^{-2}

——— Least squares fit to points on linear portion of graph.

— — — Curve of growth for a = 0.55. This corresponds to a self broadening cross-section of 4.5 x 10^{-15} cm^2.

Figure 3: Curves of growth for the (2,0) and (3,0) bands of the electric guadrupole component of the Lyman-Birge-Hopfield system of N_2. Key as for figure 3.

Table 1. f-values for the CO Fourth Positive System

v'	$f_{v',o}$	$q_{v',o}$	$f_{ee}=\frac{f_{v',o}}{q_{v',o}}$	$t_{v'}$(nsec)	$\lvert R_e^{nm}\rvert$(a.u.)
3	$(2.42\pm0.15)\times10^{-2}$	1.81×10^{-1}	0.134 ± 0.0009	7.6 ± 0.5	0.80 ± 0.04
4	$(1.52\pm0.15)\times10^{-2}$	1.19×10^{-1}	0.128 ± 0.012	8.4 ± 0.8	0.77 ± 0.05
5	$(1.07\pm0.14)\times10^{-2}$	6.88×10^{-2}	0.156 ± 0.014	7.2 ± 0.7	0.85 ± 0.06
6	$(6.0\pm0.8)\times10^{-3}$	3.67×10^{-2}	0.163 ± 0.014	7.2 ± 0.6	0.86 ± 0.05
7	$(3.2\pm0.4)\times10^{-3}$	1.84×10^{-2}	0.175 ± 0.022	7.1 ± 0.9	0.88 ± 0.08
8	$(1.27\pm0.13)\times10^{-3}$	8.9×10^{-3}	0.143 ± 0.014	9.1 ± 0.9	0.79 ± 0.06

Table 2. f-values for the Magnetic Dipole Component of the N_2 Lyman-Birge-Hopfield System[a]

v'	$10^7 f_{v',o}$	$q_{v',o}$	$10^6 f_{ee}$	$10^5 f_{v'}(\text{sec})$	$10^4 \lvert R_e^{nm} \rvert_D$
0	3.9 ± 0.3	4.31×10^{-2}	9.0 ± 0.6	9.4 ± 0.6	6.0 ± 0.6
1	12.8 ± 1.6	1.155×10^{-1}	11.1 ± 1.4	7.9 ± 1.0	6.6 ± 1.1
2	16.3 ± 1.3	1.707×10^{-1}	9.6 ± 0.8	9.5 ± 0.8	6.0 ± 0.7
3	16.5 ± 1.5	1.832×10^{-1}	9.0 ± 0.8	10.4 ± 1.0	5.8 ± 0.7
5	9.8 ± 0.7	1.217×10^{-1}	8.1 ± 0.6	12.5 ± 0.9	5.4 ± 0.6
6	7.9 ± 1.1	8.30×10^{-2}	9.5 ± 1.3	10.9 ± 1.5	5.8 ± 0.6

[a] These measurements were made on the P, Q and R branches. The combinations due to the electric quadrupole ccmponent was removed using Chin's[9] line strengths, and taking a mean value of 0.076 for $(f_{ee})_Q/(f_{ee})_D$.

Table 3. f-values for the Electric Quadrupole Component of the N_2 Lyman-Birge-Hopfield System[a]

V'	$10^8 f_{v',o}$	$10^7 f_{ee}$	$t_{v'}$(msec)	$\lvert R_e^{nm} \rvert_Q$(a.u)
1	6.6 ± 0.5	5.7 ± 0.4	1.9 ± 0.1	2.54 ± 0.13
2	11.1 ± 0.5	6.5 ± 0.3	1.8 ± 0.1	2.59 ± 0.07
3	13.0 ± 3.6	7.1 ± 2.0	1.7 ± 0.5	2.6 ± 0.5
5	10.3 ± 0.8	8.5 ± 0.7	1.6 ± 0.1	2.72 ± 0.15
6	6.0 ± 0.5	7.2 ± 0.6	2.1 ± 0.2	2.42 ± 0.14

[a] All these measurements were made on the S branches of the bands.

Table 4. Overall Radiative Lifetime for N_2 a'Πg, and the ratios of the Electric Quadrupole and Magnetic Dipole f-values

V'	$10^5 f_{v'}$(sec)	$10^2 \frac{(f_{v',o})_Q}{(f_{v',o})_D}$	$10^{12} \frac{\lvert R_e^{nm}\rvert_Q^2 (cm^2)}{\lvert R_e^{nm}\rvert_D^2}$
0			
1	7.6 ± 1.0	5.2 ± 0.8	3.5 ± 0.5
2	9.0 ± 0.8	6.8 ± 0.6	4.4 ± 0.4
3	9.8 ± 1.0	8.1 ± 2.0	4.9 ± 1.4
5	11.6 ± 0.9	10.5 ± 1.2	6.1 ± 0.7
6	10.4 ± 1.5	7.6 ± 1.2	4.2 ± 0.7

Table 5. $|R_e^{nm}|$ (atomic units) for the CO Fourth Positive System

V'	a	b	c
0	0.64	-	0.93
1	0.65	0.78	0.95
2	0.65	0.83	0.98
3	0.64	-	1.03
4	0.67	-	1.09
5	0.67	-	1.12
6	-	-	1.19
7	-	-	1.22
8	-	-	1.23

[a] Phase shift measurements.[15] The $|R_e^{nm}|$ values quoted in reference 15 have been redefined and multiplied by $\sqrt{2}$ (see appendix).

[b] Shock tube absorption measurements[16] (J = 30 - 60).

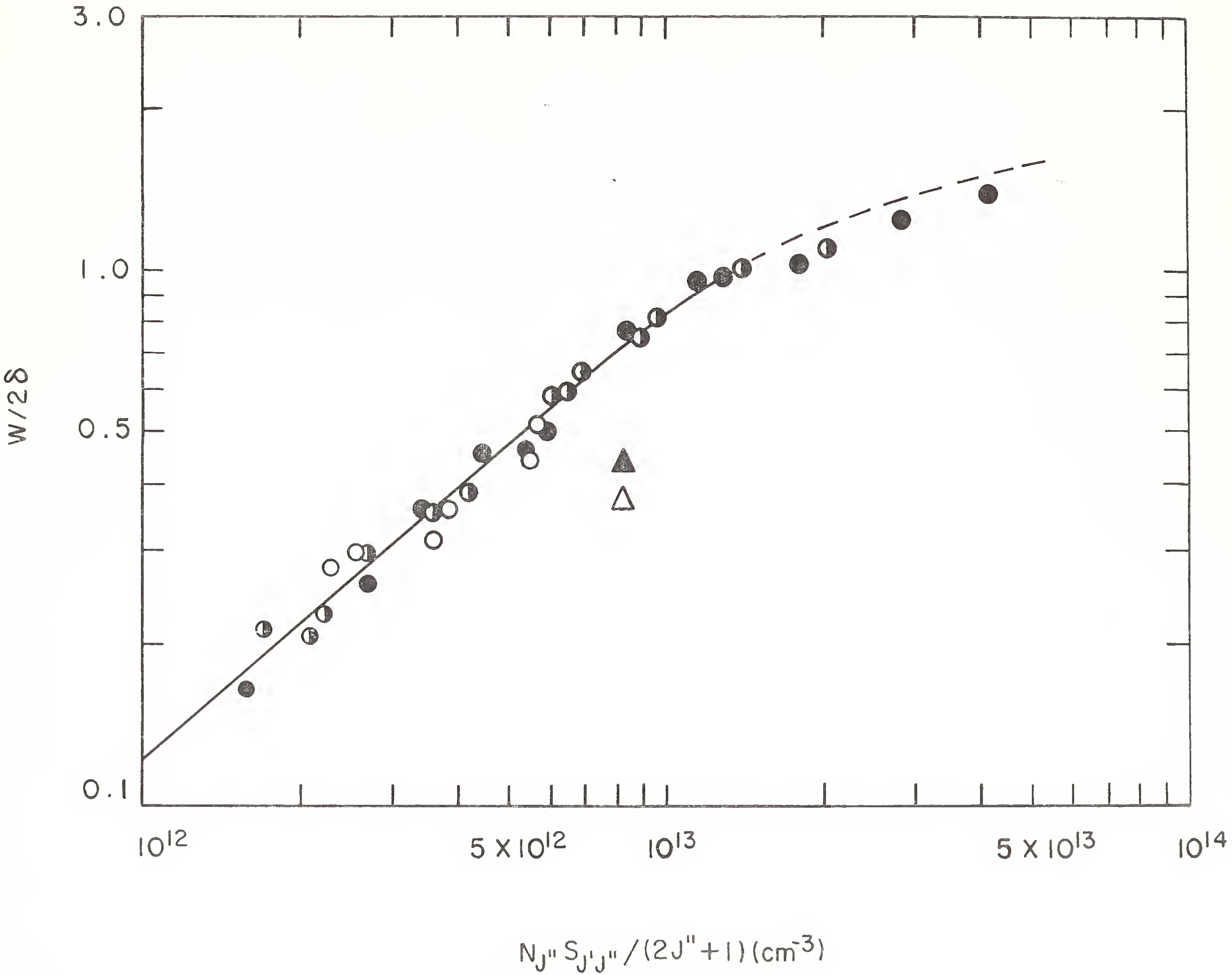
[c] Electron impact spectroscopy.[17]

Table 6. $|R_e^{nm}| \times 10^{11}$ (Bohr magnetons) for the Magnetic Dipole Component of the N_2 Lyman-Birge-Hopfield System

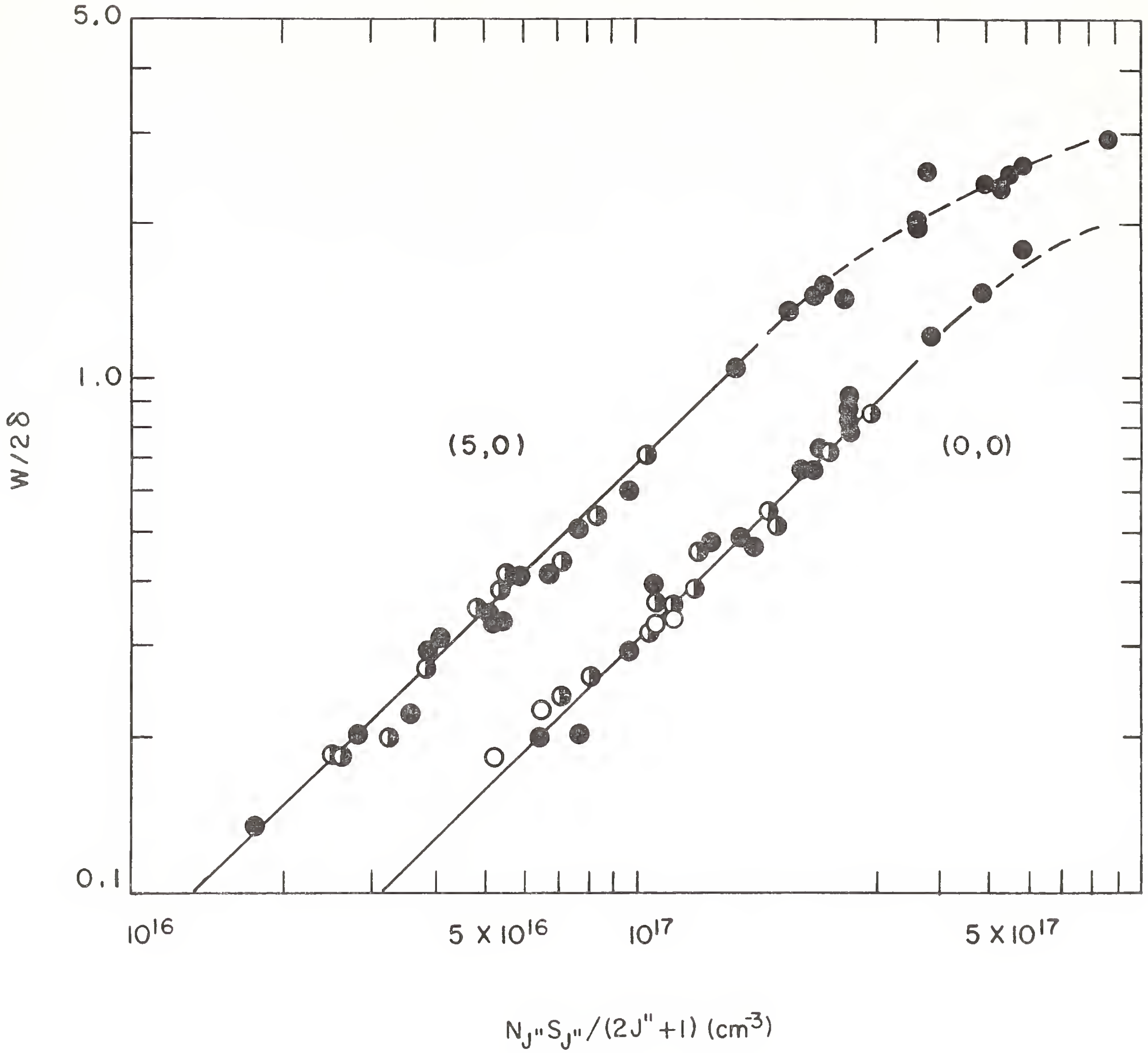
V'	a	b
0	4.2	10.6
1	5.5	9.7
2	4.8	9.2
3	4.5	9.3
4	5.1	10.4
5	4.6	10.3
6	4.8	11.7

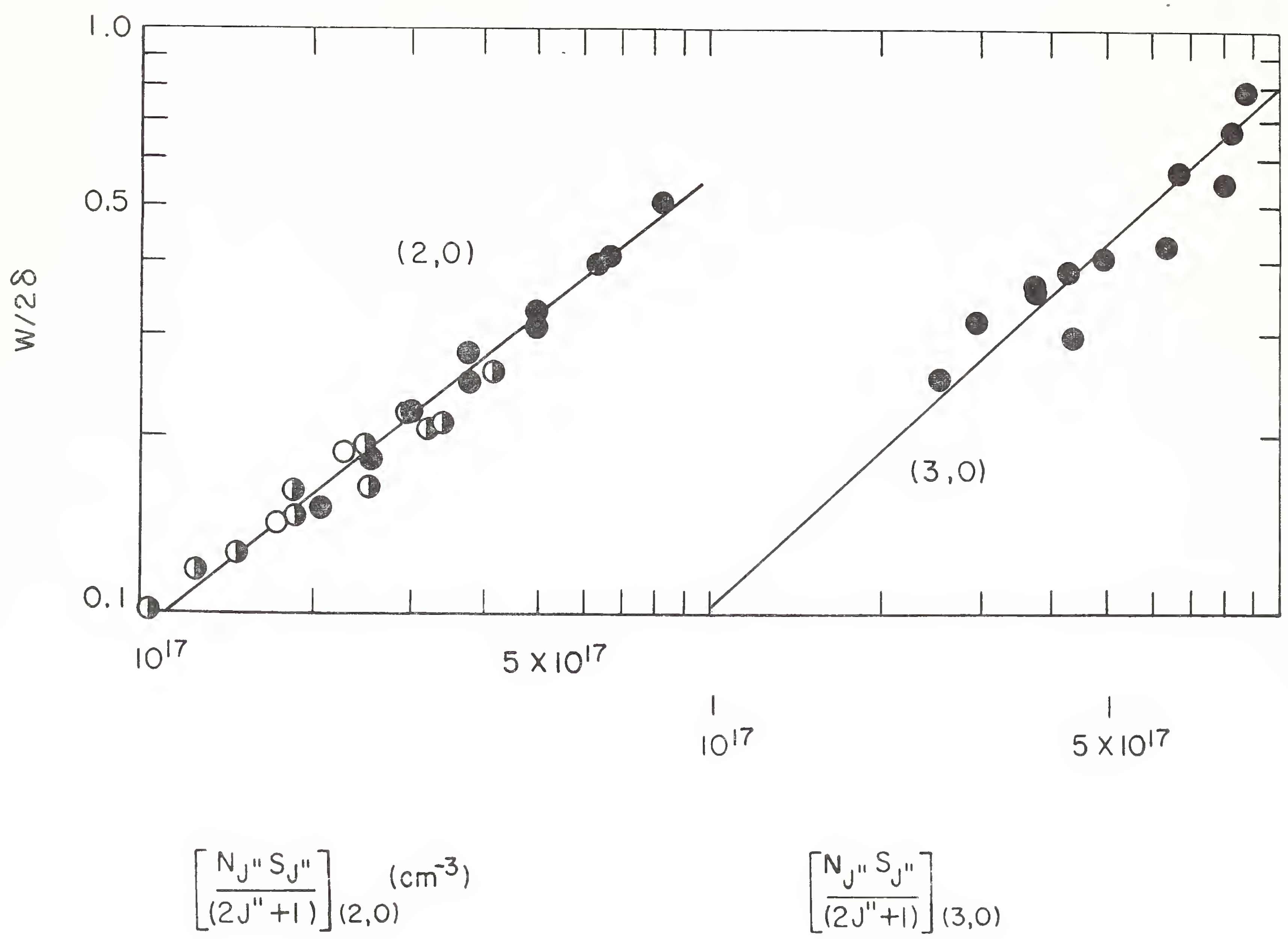
[a] Low resolution, low pressure absorption spectroscopy.[14] The D^2 values given in reference 14 have been multiplied by 4, and converted to $|R_e^{nm}|_D$ (see appendix).

[b] Low resolution, high pressure spectroscopy.[25]



3.0
1.0
0.5
0.1
W/2δ
10^12
5 X 10^12
10^13
5 X 10^13
10^14
N_J" S_J'J" /(2J"+1) (cm^-3)


5.0
1.0
0.1
W/2δ
(5,0)
(0,0)
10^{16}
5×10^{16}
10^{17}
5×10^{17}
$N_{J''}S_{J''}/(2J''+1)$ (cm^{-3})


1.0
0.5
0.1
W/2δ
(2,0)
(3,0)
10¹⁷
5 X 10¹⁷
10¹⁷
5 X 10¹⁷
$\left[\frac{N_{J''} S_{J''}}{(2J''+1)}\right]_{(2,0)}$ (cm⁻³)
$\left[\frac{N_{J''} S_{J''}}{(2J''+1)}\right]_{(3,0)}$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