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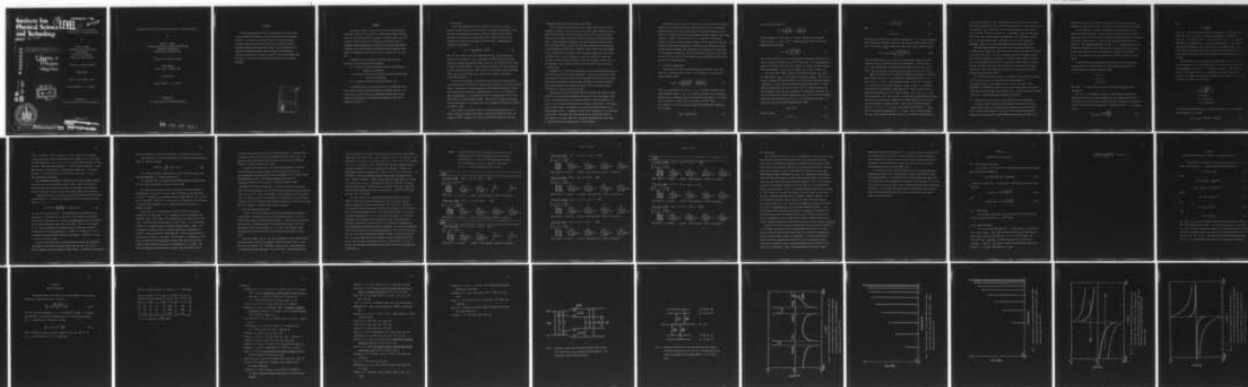
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Stark Shifts in Diatomic Molecules

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Robert W. Gammon
Institute for Physical Science
and Technology

University of Maryland
College Park, Maryland 20742

Contract No. F44620-76-C-0033

FINAL REPORT

1 Sept. 1975 - 30 Sept. 1976

Program Manager: J. H. Hinkel

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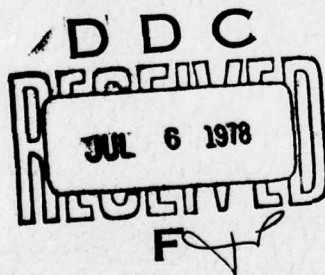


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Abstract

Standard perturbation results are applied to the case of laser induced dynamic Stark shifts of vibration-rotation terms of diatomic molecules. For fields at frequencies near an allowed vibration-rotation transition there are just four terms coupled by allowed transitions which cause significant shifts. After discussion of the method of calculating specific matrix elements from rotationless Einstein A coefficients, examples are given of Stark shift predictions for terms of HF, DF and CO involved in strong laser lines of these molecules.

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PREFACE

This report contains essentially all of the results obtained under this contract. We were able to establish the specific form of the laser-induced Stark shifts in diatomic molecular terms, to locate suitably reduced intensity data (Einstein coefficients) for the originally proposed molecules (to obtain the necessary dipole matrix elements), and to make specific calculations of the frequency dependence and magnitude of the effect in these molecules (HF, DF, and CO).

In addition to the principal investigator the following personnel were associated with the project:

W. M. Benesch, Institute for Physical Science and Technology,
University of Maryland

T. D. Wilkerson, Institute for Physical Science and Technology,
University of Maryland

R. S. Klingbeil, Systems Planning and Analysis, Inc.

A trimmed version of the present report is in preparation for the Journal of Quantitative Spectroscopy and Radiant Transfer. An initial report of the results was presented as paper W1A.1 at the International Conference on Multiphoton Processes, University of Rochester, June 1977.

I. Introduction

One of the consequences of the availability of tunable lasers has been the revival of interest in the subject of resonance fluorescence. With this have come numerous theoretical calculations, notably Mollow (1969), showing that the emission and absorption spectra lines are split by the presence of an intense monochromatic radiation field. The splitting on resonance is found to be

$$\pm \Omega = \pm (\vec{\mu}_{ij} \cdot \vec{E}) / (hc) \quad (\text{cm}^{-1}) \quad (1)$$

with $\vec{E}$ the incident laser field amplitude and $\vec{\mu}_{ij}$ the dipole matrix element of the transition. This splitting can be identified with the Rabi frequency of population inversion (Rabi, 1937) and the "dynamical Stark shift" of Autler and Townes (1955). Very beautiful confirmation of the calculations has been demonstrated with Na atomic fluorescence by Schuda, Stroud and Hercher (1974), Wu, Grove and Ezekiel (Wu, (1975), Grove, (1977)) and Walther's group (Hartig, 1976).

In earlier work Russian investigators had anticipated the importance of laser induced Stark shifts, even for non-resonance cases, due to the high available fluxes. The subject is nicely reviewed by Bonch-Bruevich and Khodovoi (1967). They continued their work and demonstrated large (.1 to 2.5 cm^{-1}) shifts of the potassium atomic D fluorescence line for Ruby illumination of 30 to 300 MW/cm^2 intensity (Bonch-Bruevich, 1969). There is even a quantum electronics textbook description of the effect with order-of-magnitude estimates in Pantell and Puthoff (1969).

More recently the powerful output of a CO_2 TEA laser has been used to produce large non-resonant Stark shifts in the excited states of atomic He (Prosnitz, 1976). Shifts of 2 to 4 $\text{\AA}^0$ at 4713 $\text{\AA}^0$ were observed for incident

intensities having amplitudes of 130 to 215 kV/cm.

Much less work has been done for case of laser induced Stark shifts in molecules, despite the fact that the most powerful lasers themselves run on molecular transitions. Braun and Petelin (Braun, 1974) calculated Stark shifts for CO_2 irradiated diatomic molecule rotation and vibration-rotation states. They estimated splitting of the lowest vibrational levels of HCl of $.1 \text{ cm}^{-1}$ and of CO of $.2 \text{ cm}^{-1}$ for a CO_2 laser running at 9.9 microns with a field amplitude of 10^6 V/cm (1.3 GW/cm^2). These shifts are quite significant, considering the narrowness of the transitions themselves, but are not as large as will occur at resonance, a case not considered by Braun and Petelin. Fedorov and Makarov (Fedorov, 1975) have published a short note on the resonance case in diatomic molecules but the form of their results is not easily used.

Aldridge et al. (1976) have attempted to estimate dynamical Stark effects in their studies of laser isotope separation. They used the results of Braun and Petelin for the non-resonant case and attempted to use the ideas of power broadening to estimate the resonant splitting under the mistaken assumption that the appropriate Rabi frequency is given by the static dipole moment. This leads to a large overestimate for HCl.

There has also been an extensive effort to calculate the effect of laser fields on the emission and absorption of a gas such as a laser medium. This work is reviewed by Beterov and Chebataev (Beterov, 1975) who point out the parts of the calculated lineshapes due to dynamical Stark effect. Particularly notable is the paper of Skribanowitz, Kelly and Feld (1972) who show calculated examples of the M (magnetic quantum number) dependence of the splitting in molecules. Typically these calculations are for fields such that the splittings are not much larger than the Doppler linewidths and so are aimed at laser induced line-narrowing spectra (hole burning).

The purpose of this report is to give the form of the dominant dynamical Stark shift on diatomic molecule vibration-rotation terms in conventional molecular notation and present some explicit calculated examples of these shifts as a function of incident laser frequency as the frequency goes through resonance. Contact is made with the 2×2 , degenerate perturbation results used in the atomic resonance case and they are applied to molecules. We attempt to treat very carefully the calculation of the appropriate dipole transition matrix elements from tabulations of the Einstein A coefficients of the molecular transitions. The examples chosen correspond to high power lines of HF, DF and CO lasers where large Stark shifts should occur but as yet have not been reported.

II. Theoretical Background

The conventional form of the off-resonance level shift of the n th level for an applied electric field $\vec{\epsilon} = \vec{\epsilon}_0 \cos(kx - \omega t)$ can be written (Bonch-Bruevich, 1967),

$$\Delta E_n(\omega) = \frac{1}{4} \sum_m \left\{ \frac{|\vec{\mu}_{mn} \cdot \vec{\epsilon}_0|^2}{E_n - E_m - \hbar\omega} + \frac{|\vec{\mu}_{mn} \cdot \vec{\epsilon}_0|^2}{E_n - E_m + \hbar\omega} \right\}, \quad (2)$$

with E_m the energy of the m th level, μ_{mn} the dipole transition matrix element between levels m and n . Because of the tradition in molecular spectroscopy of giving the spectral constants in "wave number" units (cm^{-1}) it is convenient to rewrite this as the shift of the n^{th} term, $\delta\nu_n = \Delta E_n / (hc)$. It is also useful to define transition Rabi frequencies in cm^{-1} units,

$$\Omega_{mn} = |\vec{\mu}_{mn} \cdot \vec{\epsilon}_0| / (hc). \quad (3)$$

Eq. (2) can be rewritten as

$$\delta v_n = \frac{1}{4} \sum_m \left\{ \frac{\Omega_{mn}^2}{v_n - v_m - v} + \frac{\Omega_{mn}^2}{v_n - v_m + v} \right\}, \quad (4)$$

with the energy of the n th term v_n and the frequency of the applied radiation field v , both in cm^{-1} . Combining the two terms in the curly brackets in Eq. (4) gives

$$\delta v_n = \frac{1}{2} \sum_m \frac{\Omega_{mn}^2 (v_n - v_m)}{(v_n - v_m)^2 - v^2}. \quad (5)$$

The functional form in Eq. (5) shows directly the specific character of the signs of each m^{th} contribution to the n^{th} term shift. This sign depends on whether the driving field frequency is smaller or larger than the transition frequency magnitude $|v_n - v_m|$ and on whether v_m is below or above v_n .

For terms spaced widely compared to the Rabi frequencies Ω_{mn} , and v not closer than $5 \Omega_{mn}$ to the transition frequency $|v_n - v_m|$, Eq. (5) is an accurate expression of the term shifts. We will see below that the allowed transitions to a given term have frequencies differing by 20 cm^{-1} or more while the Rabi frequencies are less than 1 cm^{-1} for intensities less than 10^8 Watts/cm^2 so that near exact resonance of a particular transition, the other terms make less than 1% contribution to the shift and we may accurately replace the resonant contribution to δv_v with the result from the 2×2 degenerate matrix calculation (Bonch-Bruevich, 1967),

$$\delta_{nm} = -\delta/2 \quad (6)$$

where we define

$$\delta = \Omega' - \Delta, \quad (7)$$

$$\Omega' = \sqrt{\Delta^2 + \Omega_{nm}^2}, \quad (8)$$

and

$$\Delta = |\nu_n - \nu_m| - \nu. \quad (9)$$

The sign of the square root is taken as the sign of Δ . Ω' is the off-resonance Rabi frequency of population inversion. Note that the maximum shift occurs at $\Delta = 0$ and is $\pm \Omega_{nm}/2$. Thus very close to the n - m^{th} resonance we have

$$\delta \nu_n = \delta_{nm} + \frac{1}{2} \sum_{m' \neq m} \frac{\Omega_{m'n}^2 (\nu_n - \nu_{m'})}{(\nu_n - \nu_{m'})^2 - \nu^2}, \quad (10)$$

with the dominant term δ_{nm} having the resonance limit $\pm(\Omega_{nm})/2$ and the remaining terms contributing a non-resonant background. The full width in Δ for reaching half the maximum resonance shift is easily shown to be $3\Omega/2$. Thus the resonance region covers the range in Δ from $-3/4\Omega$ to $+3\Omega/4$.

Figure 1 illustrates on an energy level diagram the approach to resonance when the shift in level n is dominated by resonance with level m as Δ goes to zero. δ and Ω' are as defined in Eqs. (7) and (8). As drawn, ν is less than the transition frequency $|\nu_n - \nu_m|$ so that Δ is positive. The n th level is repelled and pushed down by $\delta/2$ while the m th level is repelled and pushed up by $\delta/2$. Photon levels at $\nu_m + \Delta$ and $\nu_n + \nu$ are also displaced by $\delta/2$. Thus the pair of terms of the irradiated molecule has been split into four terms by the presence of the light field and there are four allowed transitions possible as shown: two at the irradiation frequency ν and two at $\nu \pm \Omega'$. As Δ goes to zero, each term is split by $\delta = \Omega_{nm}$ and the transition frequencies are ν , $\nu \pm \Omega_{nm}$. In the resonance region the split terms represent "dressed atoms", i.e. a mixture of the molecular

state and the radiation field. The molecular part of the split term changes from being predominately in the down (up) shifted part of the lower (upper) term as ν approaches $|\nu_{mn}|$ from below. At resonance the molecular part of the state is equally in the split terms. As ν goes above $|\nu_{mn}|$, the molecular part of the state shifts rapidly to predominately in the up (down) shifted part of the lower (upper) term. The width in Δ of this crossover is $\pm(.31)\Omega_{mn}$ around $\Delta=0$. This is discussed in Courtens and Szoke (1977).

The above light induced terms can be seen in spontaneous emission as a triplet (Grove, 1977) and at low fields with a tuned probe beam in absorption as a triplet (Wu, 1977). The term splittings could be individually studied by observing in emission or absorption a transition which began or ended on one of the resonantly split terms, in which case a doublet would be observed. The term splitting observation was anticipated in a calculation by Mollow (1972) and a first laser experiment reported in the photoionization of Na by Moody and Lambropoulos (1977).

For convenience we have collected in Appendix A some numerical conversion factors useful for laser induced Stark shift calculations. In this report the key to the frequency scale of shifts is to note that a $100 \text{ MW/cm}^2 = 10^8 \text{ Watt/cm}^2$ incident intensity beam corresponds to an electric field amplitude of 275 KV/cm or 915 Stat Volt/cm. The Rabi frequency for such a field for a 1 Debye dipole matrix element is 4.60 cm^{-1} .

III. Application of the Theory of Stark Shifts to Diatomic Molecules.

In order to apply the theory to any species we must reduce the term (energy levels) values, the selection rules, and the transition intensity data to dipole matrix elements. The data is not uniformly available for molecules but for the cases of the diatomic molecules used in lasers it is

possible to collect the necessary constants from the literature and so to evaluate the Stark shifts of Eqs. (5) and (8) for illustrative specific cases.

It is traditional to follow the notation of Herzberg (1950) for the molecular spectral constants. We here consider diatomic molecules in their ground electronic states for which the vibration-rotational terms are labeled by vibrational quantum number v and rotational (angular momentum) quantum number J . The standard expressions for the v, J labeled terms are given in Appendix B together with the spectroscopic constants used in this report. We note here that these terms are degenerate in magnetic quantum number $M_J = M$. As we discuss below this degeneracy is removed in applied electric fields.

We assume that the selection rules for diatomic molecule transitions are the same as the selection rules for dipole allowed transitions of a rotating harmonic oscillator (Herzberg, 1950):

$$\Delta v = 0, \pm 1$$

$$\Delta J = \pm 1$$

$$\Delta M = 0, \pm 1 \quad .$$

Thus each v, J term is coupled to six other terms by dipole allowed transitions.

The $\Delta v = 0$ transitions correspond to pure rotational transitions. Though they have large transition moments from the static dipole moment of the molecule, they are far off resonance for optical radiation at frequencies near the vibration rotation frequencies. Using Eq. (5) with $v \gg |v_n - v_m|_{\text{rot.}}$ we have

$$(\delta v_{v,J})_{\text{rot.}} \approx \frac{1}{2} \Omega^2 \left(\frac{2B_v}{v^2} \right) \quad (11)$$

with

$$\Omega^2 = \frac{1}{3} \left(\frac{\mu \epsilon}{hc} \right)^2$$

and $\mu = \mu_0$, the static dipole moment of the molecule. As an example consider DF with $\mu_0 = 1.82$ D, in light of intensity of 10^8 W/cm². In this case $\Omega = 4.83$ cm⁻¹ and $\delta\nu = 2.8 \times 10^{-5}$ cm⁻¹ for $\nu = \omega_e = 2998$ cm⁻¹. This shift is independent of J and weakly dependent on ν . It is much smaller than the Doppler width of the vib.-rot. transitions in DF. The molecules HF and CO give smaller shifts and so the pure rotational ($\Delta\nu = 0$) contribution to the Stark shifts will be neglected in the following calculations.

The remaining four transitions which couple terms to the ν, J term are illustrated in Fig. 2 and numbered 1 to 4. In the conventional notation the transitions are labeled P if the upper state has J decreased by 1 and R if the upper state has J increased by 1 and the lower state J is given. We augment this notation by adding the lower state ν to identify the band. This gives the notations:

	$\nu'' \begin{Bmatrix} P \\ R \end{Bmatrix} (J'')$
1	$\nu P(J)$
2	$\nu R(J)$
3	$(\nu-1)P(J+1)$
4	$(\nu-1)R(J-1)$

We can label the transitions in our calculations with $i = 1$ to 4 and the term differences $\Delta\nu_i$ where

$$\Delta\nu_i = \nu_n - \nu_m = T(\nu'', J'') - T(\nu_i, J_i). \quad (12)$$

and Rabi frequencies $\Omega_i = \Omega_{mn}$ with the label n referring to the v, J term and m the appropriate term for $i = 1$ to 4. The magnitudes of the transition frequencies order as $|\Delta v_1| < \Delta v_3 < |\Delta v_2| < \Delta v_4$. Thus the general case for diatomic molecules in the vib.-rot. band region takes the form of Eq. (5) with just four terms and a fixed order of transitions.

An example of the full range of term shifts is shown for the term $v'' = 2, J'' = 10$ of DF in Fig. 3 as a function of the applied (laser) radiation frequency at an intensity of 10^8 W/cm^2 . Notice that this plot combines the sign of the shift with a log scale by overlapping the δv scales at $\pm 10^{-6} \text{ cm}^{-1}$. Fig. 3 shows that the resonant shifts are $> .1 \text{ cm}^{-1}$ going from small negative values for low v to small positive values for large v , with sign changes at each resonance. The pattern shown in Fig. 3 will be the same for all diatomic molecules: only the specific frequencies and on-resonance shift magnitudes will change with molecule and term considered. We will return to the discussion of the meaning of the sign changes in the resonance region after we take up the question of the proper choice and calculation of transition matrix elements.

IV. Calculation of the Transition Dipole Matrix Element

To calculate the Stark shifts we need to know the individual transition dipole matrix elements for the four vib.-rot. transitions which couple to each term v, J . Specifically, we need the squared matrix elements denoted:

$$\langle v, J, M | \vec{\mu}(\vec{r}) \cdot \vec{\epsilon}_0 | v+1, J+1, (M+0, +1) \rangle .$$

In the calculations here we take the specific case of linearly polarized light with $\vec{\epsilon}_0$ parallel to z . This corresponds to the matrix elements

$$\langle v, J, M | \mu_z | v+1, J+1, M \rangle | \vec{\epsilon}_0 | ,$$

since the z component of the dipole operator gives non-zero matrix elements only for $\Delta M = 0$. The angular integrals of the rotational states are known and can be done explicitly (Townes (1955) and Penner (1959)) leaving only a radial integral as a common factor. Thus one writes

$$|\langle v, J, M | \mu_z | v+1, J+1, M \rangle|^2 = G(m, M) |\langle v, J | \mu(r) | v+1, J' \rangle|^2 \quad (13)$$

where

$$G(m, M) = \left(\frac{m^2 - M^2}{4m^2 - 1} \right) \quad (14)$$

and

$$m = \begin{cases} -J & \text{for } J \rightarrow J-1 \\ J+1 & \text{for } J \rightarrow J+1 \end{cases} \quad (15)$$

The matrix elements $\langle v, J | \mu(r) | v', J' \rangle$ are called the radial dipole matrix elements and come from electronic wavefunctions and the average dipole moment function (Meredith, 1973). The radial dipole matrix elements are further reduced to rotationless dipole matrix elements $\langle v | \mu(r) | v' \rangle$ which are independent of J, J' . It is the rotationless dipole matrix elements which are usually tabulated in the literature. This is done by writing

$$|\langle v, J | \mu(r) | v', J' \rangle|^2 = |\langle v | \mu(r) | v' \rangle|^2 F, \quad (16)$$

where F is a function of J which is nearly unity for small J . In the present work the Oppenheimer (1926) result is used:

$$F = 1 - 4\gamma m \left[1 - \frac{5}{8} \gamma m - \frac{3}{8} \gamma \right] \quad (17)$$

where $\gamma = (2Be/we)$ and m given in Eq. (15). Discussion of improved F functions can be found in Meredith (1972) and (1973). These corrections are less important for DF and CO and so for uniformity they have not been used here. Note that the Oppenheimer F function gives increased P branch matrix elements and decreased R branch matrix elements as J increases. For high J transitions which occur in diatomic lasers the F factor gives significant corrections.

Our experimental knowledge of dipole transition matrix elements usually comes from absorption measurements (Penner, 1959). These are related to integrals across the line profiles called line strengths and are proportional through known factors to the squared radial dipole matrix elements.

Intensity measurements are often converted to spontaneous emission values called Einstein A coefficients through the use of the expression (Penner, 1959) for $v'J' \rightarrow vJ$

$$A(v'J', vJ) = \frac{64\pi^4 \nu^3 |m|}{3h(2J'+1)} |\langle v, J | \mu | v', J' \rangle|^2 \quad (18)$$

with units of (molecule-sec.)⁻¹. Though experimental absorptions may be reduced to A coefficients like $A(vJ, v'J')$ the theoretical comparisons and tables of coefficients are in terms of rotationless Einstein coefficients $A(v', v)$ which correspond to Eq. (18) for the case $|m| = 1$ (P(1) Branch, $J = 1$). The rotationless matrix elements do not correspond to any real transition but to the extrapolation of $\langle v, J | \vec{\mu} | v', J' \rangle$ versus m to $m = 0$ or taking vibrationless matrix elements to be equal to $\langle vJ | \vec{\mu} | v'J' \rangle$ at low J ($J = 0$ or 1 , R(0) or P(1)).

In the present paper the needed dipole matrix elements were calculated from tables of rotationless Einstein coefficients for HF, DF and CO found in Meredith (1973) and Herbelin (1974a, 1974b). The Einstein coefficients

used are collected in Table BII. of Appendix B. The procedure used was:

(a) Calculate the rotationless dipole matrix elements from the rotationless A coefficients using

$$\langle v|\mu|v'\rangle = \frac{3h}{64\pi^4} \frac{1}{v^3} A(v',v) . \quad (19)$$

(b) Calculate the full dipole matrix element from (a) using Eq. (16) with the appropriate F factor from Eq. (17).

(c) Calculate the z component dipole matrix elements from (h) using Eq. (13) with the appropriate G(m,M) from Eq. (14).

As a check on the results of steps (a) and (b) of this procedure, I calculated the $A(vJ,v',J')$ for the OP(10) transition in DF and found 33.7 sec.^{-1} compared to the value measured by Bonczyk (1975) of $34 \pm 4 \text{ sec.}^{-1}$. Also I calculated $\langle vJ|\mu|v'J'\rangle$ for the 4P(10) transition of CO and found a value of .239 D compared to $.238 \pm .003 \text{ D}$ measured by Weisbach and Chackerian (1973).

For a given $(v'-v'')$ band and line P(J'') or R(J'') the relative intensity of the Stark split $M \rightarrow M$ components will be determined by the function G(m,M) of Eq. (14). The contributions to the Stark shift of the v'',J'' term will also be proportional to G(m,M) when v is off-resonance so that δv is proportional to the squared matrix elements. When v is on-resonance the shift of each M labeled term will be proportional to $G(m,M)^{\frac{1}{2}}$. These two cases are illustrated for a P(10) transition in Fig. 4 (non-resonant) and Fig. 5 (resonant). The lifting of M degeneracy is well known in microwave Stark measurements (Townes, 1955) and was included in detail in the lineshape calculations of Skribanowitz et al. (1972). Note that this degeneracy lifting occurs in atoms as well as molecules and so

is always to be expected in the Stark lineshapes unless M state selection has occurred before the species are illuminated with the laser field. Its effect on laser induced Stark shift spectra lineshapes was not discussed except in the work of Grove et al. (1977).

Since the first detection of laser induced Stark shifts in molecules will probably occur in a gas inside a laser without state selection, the calculations here have been done with the maximum $\Delta M = 0$ matrix element corresponding to $M = 0$. The actual lineshapes will tend to be triangular as shown in Figs. 4 and 5. The first moments of these "lineshapes" are slowly varying with J and fall at 0.82 of the maximum shift for the non-resonant case and 0.90 of the maximum shift for the resonant case for $J = 5$ to 15. Thus, for the high J cases important in diatomic molecules at resonance, half of the intensity of a Stark shift will occur between 0.90 and 1.00 of the maximum shifted component ($M=0$) and we need only calculate the $M=0$ component to estimate the spectrum of shifts.

V. Stark Shift Calculation Results

In this section the numerical results of the calculated Stark shifts are presented. Specifically, Eqs. (5) and (8) and used with $M = \Delta M = 0$ dipole matrix elements calculated from Einstein A coefficients as described in Section IV. The overall pattern of the shifts for a term (v,J) has been shown in Fig. 3 for the term $v = 2, J = 10$. This shows the four resonances which will occur at the four transitions which couple to this term.

Since the $2P(10)$ line of DF is a strong laser line, we have the near-resonance region of this line displayed in greater detail in Fig. 6. The line occurs at 2494.37 cm^{-1} . The shifts in the $(2,10)$ term displayed on the vertical axis cover the range $\pm(1 \text{ to } 10^{-3}) \text{ cm}^{-1}$. Notice that for the

two laser intensities assumed, the off-resonance shifts vary as the intensity (10x) while the resonant shift vary as the square root of the intensity. Also indicated on the figure is the Doppler width $\delta\nu_0$ (full width at half maximum) for $\Delta v = 1$ transitions of DF. (Calculations and table of Doppler widths is given in Appendix C.) One can see that for 10^8 W/cm^2 intensity the Stark shift should be resolvable for ν within $\pm 5 \text{ cm}^{-1}$ of the 2P(10) line. At 10^9 W/cm^2 even the non-resonant shift is greater than the Doppler width over a range of $\pm 20 \text{ cm}^{-1}$. Figure 7 shows the (2,10) term shift near 2P(10) on a linear scale in the range where the shift at 10^8 W/cm^2 is greater than the Doppler width. The on-resonance term shifts are equal to half the respective Rabi frequencies at the two intensities: $.188 \text{ cm}^{-1}$ at 10^8 W/cm^2 and $.594 \text{ cm}^{-1}$ at 10^9 W/cm^2 .

For other terms of DF and other molecules the shifts are similar. Table I collects the important parameters for the lower state terms of several strong laser lines in the molecules HF, DF and CO. The lines were selected from the description of laser line strengths in the literature: DF lines from Kwok (1970) and CO lines from Yardley (1971). The lasing transition corresponds to $I = 1$ in the table. The labels $I = 1$ to 4 corresponds to the numbering of the transitions in Fig. 2 and Section III. The matrix elements are for the $\Delta M = M = 0$ transitions corresponding to the maximum shift and maximum intensity transitions. The molecular parameters used in these calculations are given in Appendix B. From this table one sees that the DF results presented graphically in Figs. 3, 6 and 7 are typical. The CO molecule has larger matrix elements and Rabi frequencies but only by 2x. The term shift at resonance with Δv_1 is given with $\Omega_1 = \pm \Omega_1/2$ and the non-resonance shift coming from the three term sum over non-resonant contributions.

Table I . Calculated resonant case Stark shifts for particular lines and terms of HF, DF and CO assuming a laser intensity of 10^8 watts/cm² $\equiv \epsilon = 275$ KV/cm. The dipole matrix element $\mu(I)$ corresponds to $|\langle v'', J'', M = 0 | \mu_z | v', J', n=0 \rangle|$ with $J'' \equiv J_2$. Δv and Ω are given in cm⁻¹, μ in esu.

HF

0 P(9) LINE, V2= 0 , J2= 9 , M2= 0 TERM

A(1 , 0) = 189.2

A(0 , -1) = 0

I	1	2	3	4
$\Delta v(I)$	-3537.35	-4273.32	3648.	4444.62
$\mu(I)$	5.80996E-20	3.89405E-20	0	0
$\Omega(I)$	.267258	.179126	0	0

TERM SHIFTS = -.133641 , .133617 WITH NON-RES. SHIFT=-1.19264E-5

1 P(10) LINE, V2= 1 , J2= 10 , M2= 0 TERM

A(2 , 1) = 322.5

A(1 , 0) = 189.2

I	1	2	3	4
$\Delta v(I)$	-3320.4	-4096.71	3429.98	4273.32
$\mu(I)$	8.26242E-20	5.29447E-20	5.99430E-20	3.89405E-20
$\Omega(I)$	.330071	.243546	.275761	.179126

TERM SHIFTS = -.189371 , .1902 WITH NON-RES. SHIFT= 1.64692E-4

DF

0 P(9) LINE, V2= 0 , J2= 9 , M2= 0 TERM

A(1 , 0) = 54.4

A(0 , -1) = 0

I	1	2	3	4
$\Delta v(I)$	-2692.08	-3089.42	2751.49	3170.92
$\mu(I)$	4.75117E-20	3.57212E-20	0	0
$\Omega(I)$	.218554	.164318	0	0

TERM SHIFTS = -.109295 , .109259 WITH NON-RES. SHIFT=-1.81559E-5

Table I (cont.)

1 P(10) LINE, V2= 1 , J2= 10 , M2= 0 TERM

A(2 , 1) = 97.3

A(1 , 0) = 54.4

I	1	2	3	4
$\Delta V(I)$	-2580.08	-3006.03	2639.04	3089.42
$\mu(I)$	6.74727E-20	4.91828E-20	4.86639E-20	3.57212E-20
$\Omega(I)$	.310375	.226241	.223854	.164318

TERM SHIFTS = -.15499 , .155384 WITH NON-RES. SHIFT= 1.96964E-4

2 P(9) LINE, V2= 2 , J2= 9 , M2= 0 TERM

A(3 , 2) = 129

A(2 , 1) = 97.3

I	1	2	3	4
$\Delta V(I)$	-2519.51	-2894.75	2580.03	2977.41
$\mu(I)$	8.06618E-20	6.06447E-20	6.74727E-20	5.10569E-20
$\Omega(I)$	.371044	.278966	.310375	.234862

TERM SHIFTS = -.185143 , .185902 WITH NON-RES. SHIFT= 3.79520E-4

2 P(10) LINE, V2= 2 , J2= 10 , M2= 0 TERM

A(3 , 2) = 129

A(2 , 1) = 97.3

I	1	2	3	4
$\Delta V(I)$	-2494.37	-2908.12	2553.92	2992.03
$\mu(I)$	8.16389E-20	5.95039E-20	6.82819E-20	5.01215E-20
$\Omega(I)$	.375539	.273741	.314097	.230559

TERM SHIFTS = -.18737 , .188169 WITH NON-RES. SHIFT= 3.99451E-4

3 P(9) LINE, V2= 3 , J2= 9 , M2= 0 TERM

A(4 , 3) = 151

A(3 , 2) = 129

I	1	2	3	4
$\Delta V(I)$	-2433.22	-2797.41	2494.37	2880.66
$\mu(I)$	9.13602E-20	6.90641E-20	8.16389E-20	6.17765E-20
$\Omega(I)$	.422557	.317695	.375539	.284172

TERM SHIFTS = -.21072 , .211837 WITH NON-RES. SHIFT= 5.58536E-4

Table I (cont.)

CO

6 P(10) LINE, V2= 6 , J2= 10 , M2= 0 TERM

A(7 , 6) = 180

A(6 , 5) = 162

I	1	2	3	4
$\Delta V(I)$	-1945.81	-2021.35	1968.03	2045.04
$\mu(I)$	1.40550E-19	1.30370E-19	1.31116E-19	1.21716E-19
$\Omega(I)$	.646532	.599702	.603134	.559295

TERM SHIFTS = -.319554 , .326977 WITH NON-RES. SHIFT= 3.71152E-3

7 P(8) LINE, V2= 7 , J2= 8 , M2= 0 TERM

A(8 , 7) = 196

A(7 , 6) = 180

I	1	2	3	4
$\Delta V(I)$	-1927.35	-1987.93	1949.75	2011.51
$\mu(I)$	1.48751E-19	1.39937E-19	1.40114E-19	1.31960E-19
$\Omega(I)$	.684254	.643709	.644526	.607014

TERM SHIFTS = -.338082 , .346172 WITH NON-RES. SHIFT= 4.04481E-3

8 P(11) LINE, V2= 8 , J2= 11 , M2= 0 TERM

A(9 , 8) = 209

A(8 , 7) = 196

I	1	2	3	4
$\Delta V(I)$	-1889.43	-1970.54	1911.65	1994.37
$\mu(I)$	1.58251E-19	1.45749E-19	1.50620E-19	1.38822E-19
$\Omega(I)$	.727953	.670445	.69295	.638583

TERM SHIFTS = -.358963 , .368991 WITH NON-RES. SHIFT= 5.01394E-3

VI. Conclusions

When this work was proposed we were concerned with the possible effects the then estimated large Stark shifts might have on the laser output spectrum, laser turn-on transients and atmospheric propagation of high intensity lasers such as some of the chemical lasers which run on diatomic molecular vibrational-rotational transitions. After careful study of the theory of these Stark shifts (Mollow, 1972a, 1972b) and the atomic Na experimental verifications it is clear that even though the terms of the molecules inside a high energy laser are surely split, the lasing emission continues to occur at the dominant component of the emission of the coupled terms which is at the natural frequency of the transition. There is spontaneous emission which will be occurring as side light with the Stark splittings but the side bands are not able to compete in stimulated emission with the stronger, unshifted component. On the propagation question, careful study of the sign of the shift given by the general equation, Eq. (5), shows that the terms always move so as to shift the molecular transition away from the incident radiation frequency. Thus any absorption line causing beam attenuation in atmospheric propagation will be Stark shifted away from the high intensity laser frequency leading to a drop in attenuation as long as some form of heating or higher order process doesn't change the population in the initial state of the near resonant transition.

The area of current technical interest which may find fruitful application of the present calculations is that of multiphoton ionization; it is clear that the high intensities used in these studies are capable of causing large shifts in energy levels (terms) of the molecule. If the multistep process depends on some intermediate step resonances then the probability for the excitation or ionization can be critically dependent on the intensity of the beam due to Stark shifts. Moody and Lambropoulos (1977) showed a simple

example for multiphoton ionization of Na. Earlier, Liao and Bjorkholm (1975) had demonstrated, at low power and high resolution, the sharp resonance in the intermediate state which could be Stark intensity tuned in two photon absorption. Papers have begun to appear on coupled one- and two-photon resonant dynamic Stark splitting (Wong, 1977).

It seems that a serious present limitation on our understanding occurs because as yet there is no demonstration of dynamic Stark shifts of laser irradiated molecules. It is hoped that the present calculations might serve to encourage some careful experiments on diatomic molecules where the spectral constants are well enough known to allow quantitative comparison of experiment and theory. It seems that any scheme which can selectively and efficiently produce desired photoionization will need to consider the dynamic Stark shifts of molecular terms.

APPENDIX A

Numerical Conversion Factors

A-I. Intensity-field Conversion

For a field $\vec{\epsilon} = \vec{\epsilon}_0 \cos(kx - \omega t)$, the average Poynting vector magnitude gives the average intensity as

$$S = |\langle \vec{S} \rangle| = \frac{c}{8\pi} |\epsilon_0|^2 \quad (\text{ergs/cm}^2) \quad , \quad (\text{A.1})$$

in cgs units. Noting that $1 \text{ Stat Volt/cm} \equiv 300 \text{ Volt/cm}$ we find the useful relations:

$$\epsilon_0 (\text{V/cm}) = 27.46 \sqrt{S (\text{W/cm}^2)} \quad , \quad (\text{A.2})$$

and

$$\epsilon_0 (\text{Stat V/cm}) = .0915 \sqrt{S (\text{W/cm}^2)} \quad . \quad (\text{A.3})$$

A-II. Dipole Units

Traditionally dipole moments and dipole matrix elements are given in units of Debye (D), where $1 \text{ D} \equiv 10^{-18} \text{ esu-cm}$.

A-III. Rabi Frequencies

In the cgs system the product of μ in esu-cm and ϵ in Stat V/cm is an energy in ergs. For a field of 915 Stat Volt/cm, corresponding to a light beam intensity of 10^8 W/cm^2 and μ of $1 \text{ D} \equiv 10^{-18} \text{ esu-cm}$, $\mu\epsilon = 915 \times 10^{-18} \text{ erg}$. Expressed as a Rabi frequency in cm^{-1} we have $\Omega_0 = (\mu\epsilon)/(hc) = 4.60 \text{ cm}^{-1}$. This result is useful in scaling other cases with different μ in Debye, and intensity S since

$$\Omega = \left(\frac{\mu(D)}{1D} \right) \cdot \left(\frac{S(W/cm^2)}{10^8} \right)^{1/2} (4.60 \text{ cm}^{-1}) .$$

APPENDIX B

Spectroscopic Notation and Constants for Diatomic Molecules

Following Herzberg (1950) we write the term value of the v (vibrational quantum number), J (angular momentum quantum number) as

$$T = G(v) + F_v(J) \quad , \quad (B.1)$$

with

$$G(v) = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 \dots \quad (B.2)$$

$$F_v(J) = B_v J(J+1) - D_v J^2(J+1)^2 + \dots \quad (B.3)$$

where

$$B_v = B_e - \alpha_e(v + \frac{1}{2}) + \dots \quad (B.4)$$

and

$$D_v = D_e + \beta_e(v + \frac{1}{2}) + \dots \quad (B.5)$$

with

$$D_e = 4 B_e^3 / \omega_e^2 \quad . \quad (B.6)$$

ω_e , $\omega_e x_e$, B_e , α_e are tabulated in Hertzberg (1950) and more recently in the A.I.P. Handbook (Gray, 1972). β_e is much less than D_e so we neglect it and all the higher terms in anharmonicity and vibration-rotation coupling. The spectral constants used in this paper are collected in Table B-I for the molecules HF, DF and CO. The Einstein coefficients (rotationless) for the $\Delta v = 1$ transitions used in this paper are collection in Table B-II.

Table BI. Spectroscopic parameters used in calculations of terms^(a),
all in cm^{-1} units.

	HF	DF	CO
ω_e	4138.32	2998.19	2169.8233
$\omega_e x_e$	89.88	45.76	13.2939
B_e	20.9557	11.000	1.931271
α_e	.798	.2907	.017513
$D_e^{(b)}$	2.149(-3)	5.923(-4)	6.120(-6)

(a) From Gray (1972).

(b) $D_e = 4B_e^3/\omega_e^2$.

Table BII. Rotationless Einstein Coefficients $A(v+1,v)$ in sec^{-1} .

v	MOLECULE		
	HF (a)	DF (b)	CO (c)
0	189.	54.4	33.4
1	322.5	97.3	64.2
2	406.1	129.	92.5
3	446.3	151.	118.
4	449.8	163.	141.
5	423.6	167.	162.
6	374.5	163.	180.
7	310.0	153.	196.
8	237.4	138.	209.

(a) From Meredith (1973).

(b) From Herbelin (1974 a).

(c) From Herbelin (1974 b).

APPENDIX C

Doppler Linewidths

The Doppler width, full width at half maximum (FWHM), of the Gaussian lineshape of a gaseous molecule is given by

$$\frac{\Delta\nu}{\nu_o} = 2 \sqrt{\frac{2R \log_e(2)}{c^2}} \sqrt{\frac{T}{M}} \quad (C.1)$$

with the transition frequency ν_o , c the velocity of light, R the molar gas constant, T the absolute temperature, and M the molecular weight. For T in Kelvin and M in gm/mole, we have

$$\frac{\Delta\nu}{\nu_o} = 7.162 \times 10^{-7} \sqrt{\frac{T}{M}} \quad (C.2)$$

Table C-I gives the values of Doppler widths for HF, DF and CO at $\nu_o = \omega_e$ corresponding to $\Delta\nu = 1$ transitions.

Table CI. Doppler widths at $T = 300$ K, $\Delta v = 1$ transitions.

Molecule	M (gm/mole)	ν_0 (cm^{-1})	$\Delta\nu$ (a) (cm^{-1})
HF	20	4138.	.011
DF	21	2998.	.008
CO	28	2170.	.005

(a) $\Delta\nu = \nu_0 (7.162 \times 10^{-7} \sqrt{T/M})$, FWHM.

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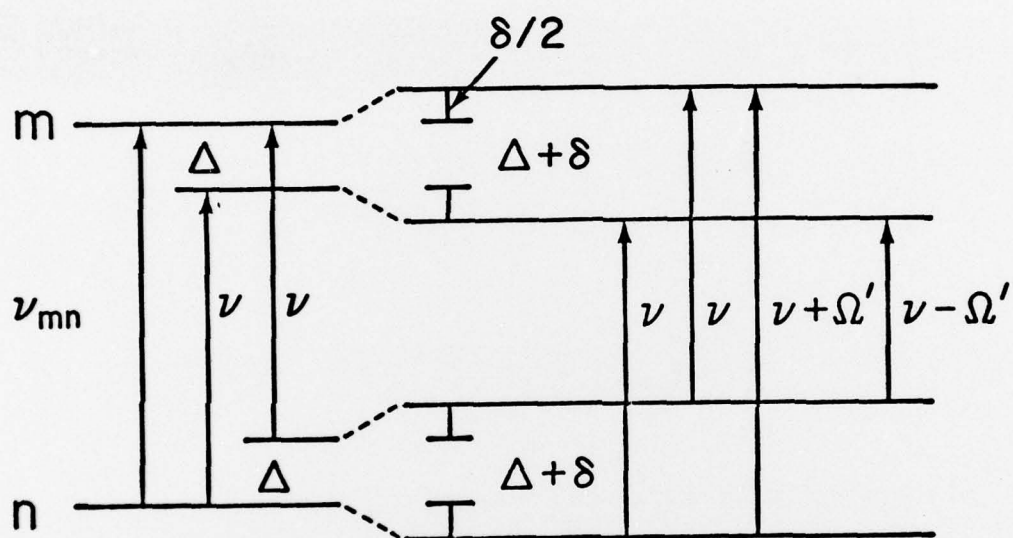


Fig. 1 Schematic energy level diagram with dynamic Stark shifts. The transition is ν_{nm} , the applied field frequency ν , the detuning Δ , and the term shifts $\delta/2$.

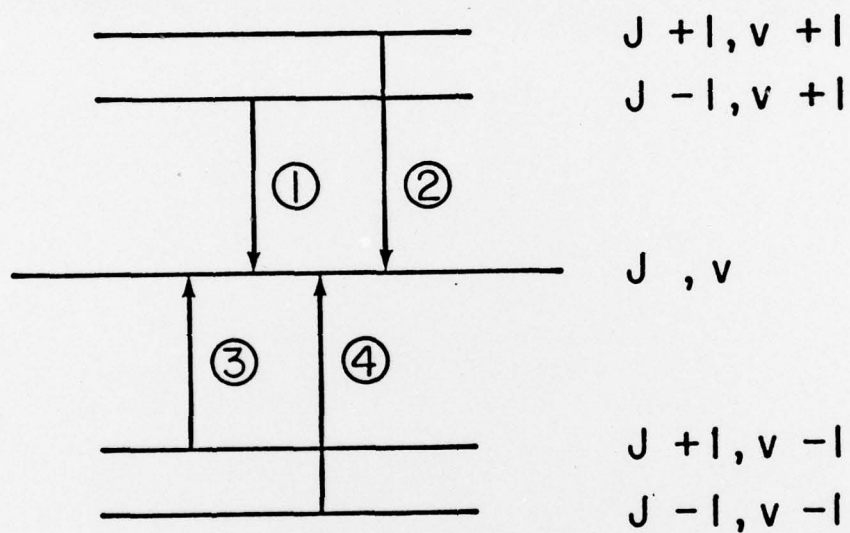


Fig. 2 Schematic diagram of the vibration-rotation terms coupled by allowed transitions to the term v, J . The numbering inside circles corresponds to the running index i 1 to 4 in the text.

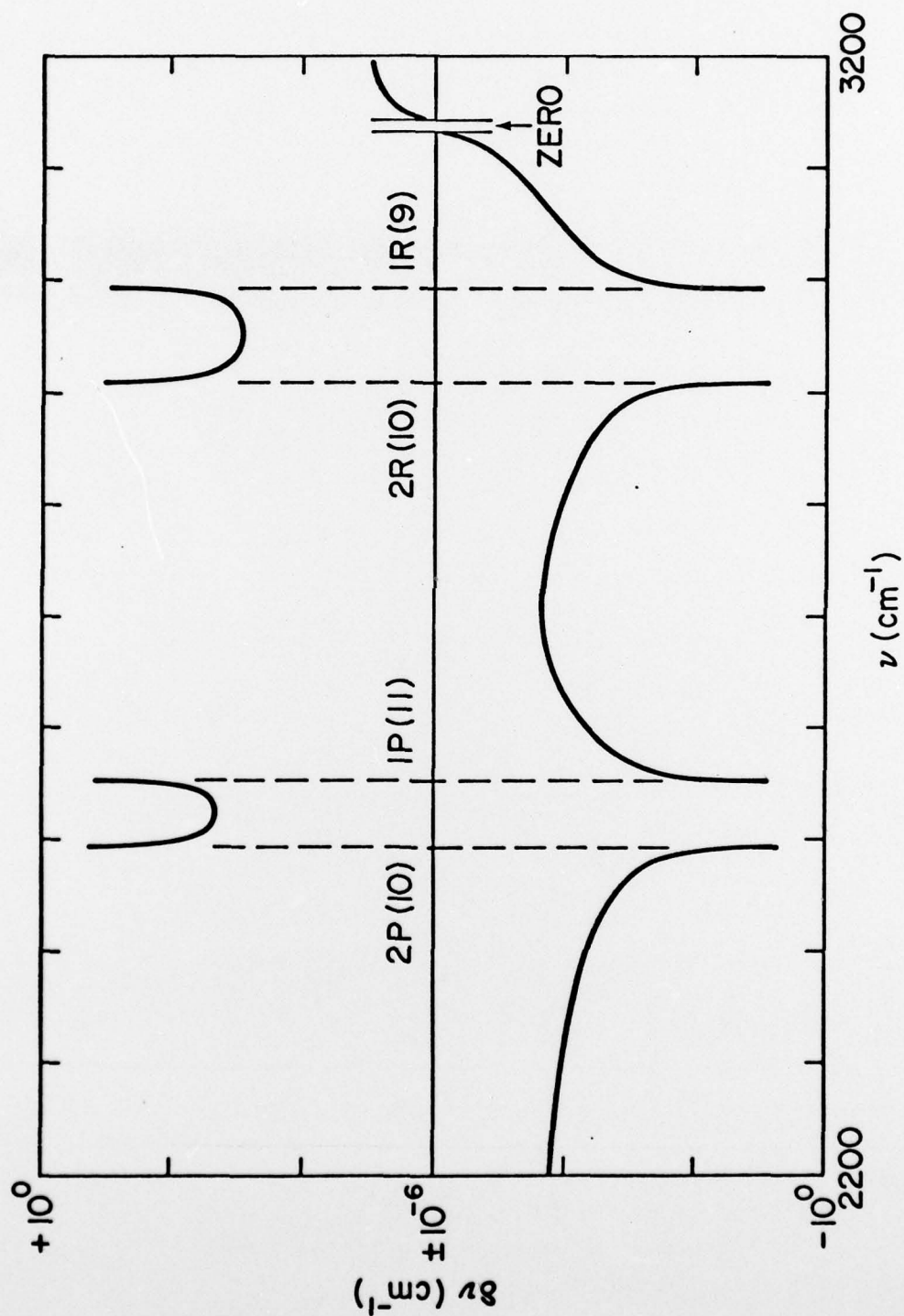


Fig. 3 Calculated dynamic Stark shifts for the term $v=2$, $J=10$, $M=0$, of DF at an incident intensity of 10^8 W/cm^2 as a function of the frequency of the radiation. Note the overlapping log scales from -1 to -10^{-6} and 10^{-6} to 1 .

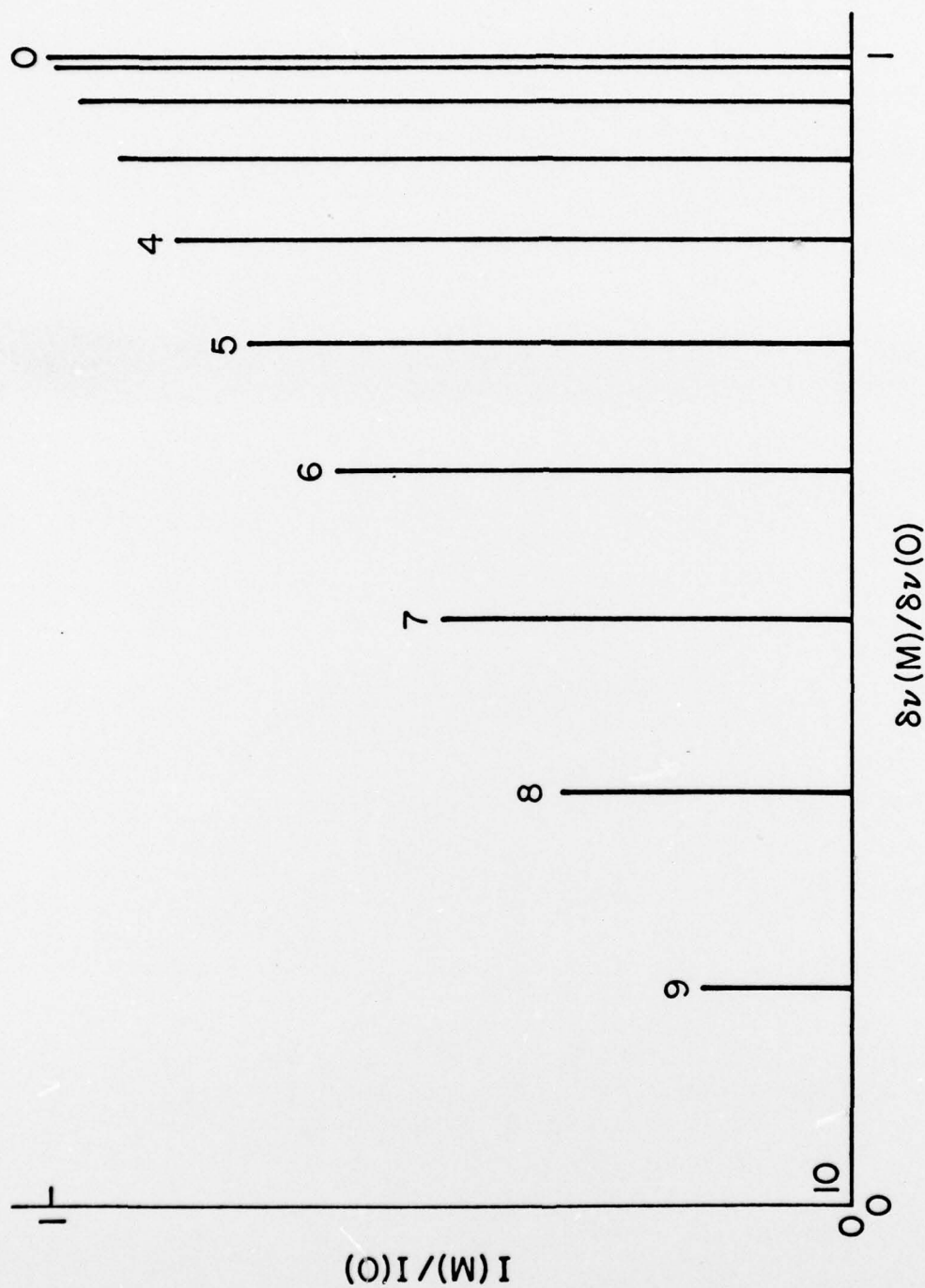


Fig. 4 Relative intensity vs. relative Stark shifts for the M components of a P(10) line $\Delta M=0$ transitions off resonance. Numbers above the lines are values of M.

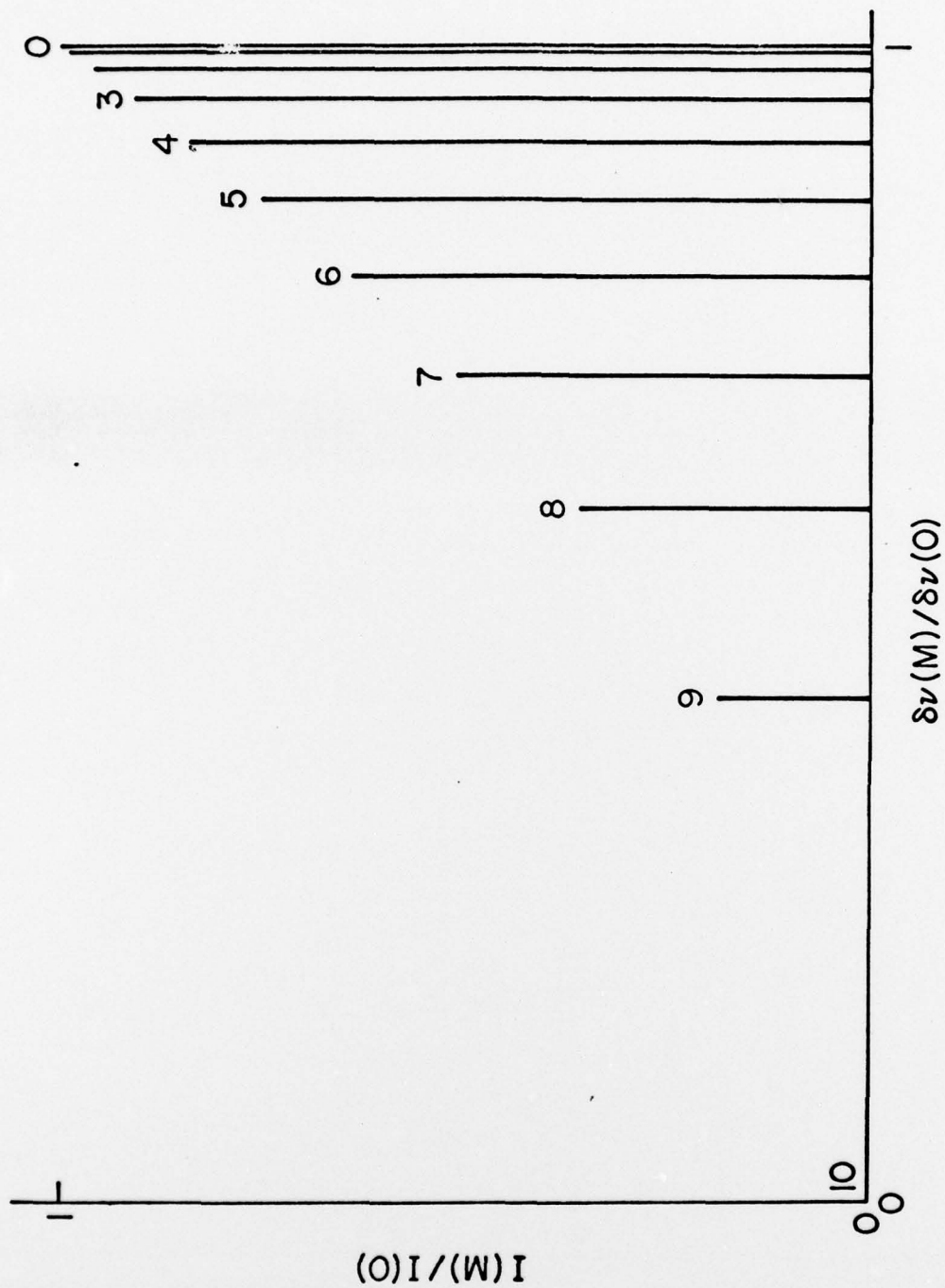


Fig. 5 Relative intensity vs. relative Stark shifts for the M components of a P(10) line $\Delta M=0$ transitions at resonance. Numbers above the lines are values of M.

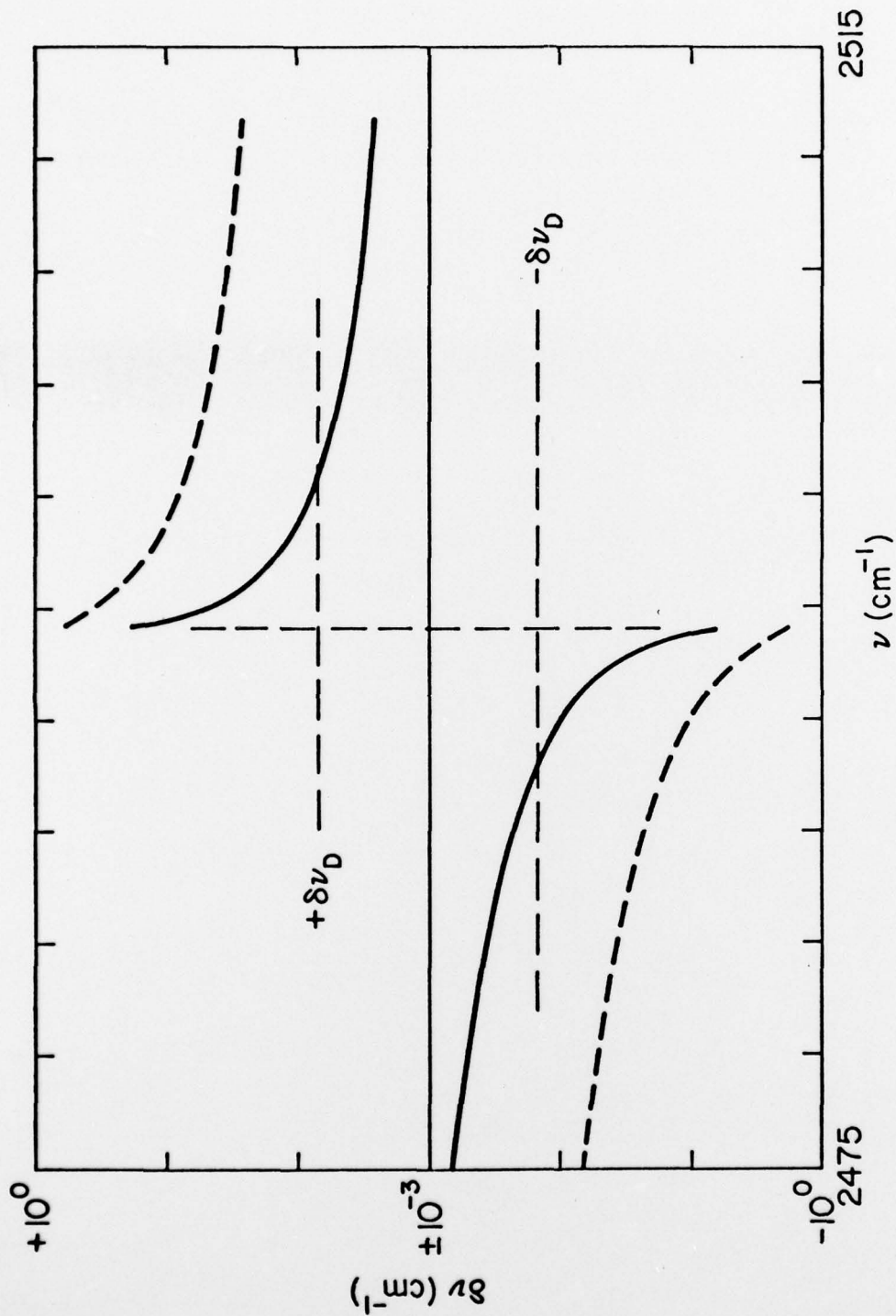


Fig. 6 Calculated dynamic Stark shifts for the term $v=2$, $J=10$, $M=0$ of DF near the $2P(10)$ transition at two intensities: solid curve for 10^8 W/cm^2 and broken curve for 10^9 W/cm^2 . The lines labeled $\delta\nu_D$ indicate the Doppler width (FWHM) for this transition at 300°K .

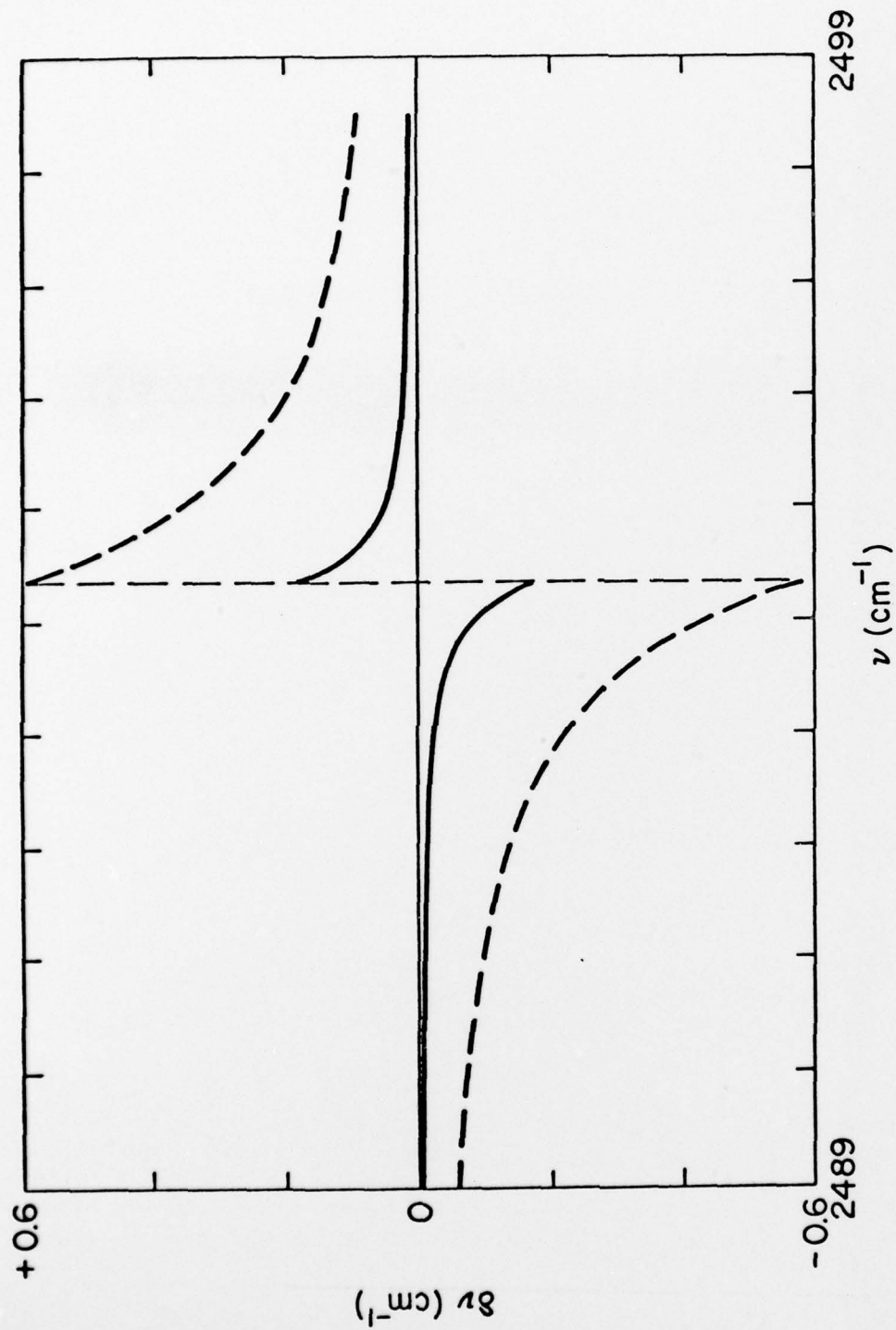


Fig. 7 Linear plot of the dynamic Stark shift for the term $v=2$, $J=10$, $M=0$ of DF near the $2P(10)$ transition at two intensities;

solid curve for 10^8 W/cm^2 and broken curve for 10^9 W/cm^2 .
The maximum shift reaches $|\Omega/2|$ with values of .157 and .594 cm^{-1} for these two intensities.

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