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Dependence of the Electronic Transition Moment on Internuclear Separation in Na₂: A Quantum Mechanical Treatment

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In this case, a new $g_2(E)$ can be determined from the Stieltjes transform of the same $H(t)$.⁴ However, g_2 would be different from g .

Equations (5) and (6) are special cases of a general representation problem:

$$H(t, E_0) = \int_0^\infty g(E) \bar{H}(t, E) dE. \quad (7)$$

In Eq. (7), if $\bar{H}(t, E)$ is linearly proportional to $H(t, E)$ in t space, then $g(E)$ is a δ function, i.e., a null distribution; if not, $g(E)$ becomes continuous. Therefore, the existence of a continuous distribution is dependent on a prior knowledge of α which determines $\bar{H}(E, t)$. In the work of Austin *et al.*, the value of α is not discussed except in their adaptation of Eq. (5) which is equivalent to assuming that $\alpha=1$. On the other hand, we found⁵ that macromolecular reactions usually involve complex kinetics; and instances are known where the reaction does not obey first-order kinetics. Without having direct physical evidence at hand, I have looked into the following problem:

Based on $H(t)$, is there a mathematical principle to determine $g(E)$ independently from $\bar{H}(t, E)$? I found the answer to be negative.⁶ Therefore, it seems that the proposed myoglobin conformer of Austin *et al.*, intuitively plausible or biologically important as it may be, is not unambiguously established.

¹R. H. Austin, K. Beeson, W. Eisenstein, H. Frauenfelder, I. C. Gunsalus, and V. P. Marshall, *Phys. Rev. Lett.* **32**, 403 (1974).

²R. H. Fowler, *Statistical Mechanics* (Cambridge Univ. Press, Cambridge, England, 1936), pp. 700–719.

³W. Primak, *Phys. Rev.* **100**, 1677 (1955).

⁴E. C. Titchmarsh, *Fourier Integrals* (Oxford Univ. Press, Oxford, England, 1949), 2nd ed., p. 317.

⁵P. H. Fang, F. C. Chao, and J. L. Tullis, *Microvascular Res.* **8**, 70 (1974).

⁶P. H. Fang, *Phys. Rev. B* **1**, 932 (1970).

Dependence of the Electronic Transition Moment on Internuclear Separation in Na₂: A Quantum Mechanical Treatment

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We present a quantum mechanical treatment of laser-induced atomic fluorescence from molecular sodium. It is shown that such fluorescence data may be analyzed with an r -centroid approximation and an accurate determination of the electronic transition moment may be made.

The proper interpretation of the optical spectra of simple molecules requires knowledge of the variation of the electronic transition moment with internuclear separation. This variation must be considered when analyzing absorption, emission,¹ and resonance Raman data.² Experimental measurements of the separation dependence of the transition moment have been scarce and have relied for the most part on r -centroid analyses of discrete vibrational spectral progressions.³ Recently Gersten⁴ has described a new technique for measuring the transition moment by monitoring the atomic fluorescence resulting after transitions from a ground electronic state to a dissociative excited state. Callender *et al.*⁵ extended this method of induced atomic fluorescence to apply to cases in which the upper electronic state has an attractive potential. Their

technique, if accurate, would appear to be preferable to previous methods in that it does not require numerical calculations of matrix elements and needs only approximate knowledge of the two potential functions involved.

In the experiments reported by Callender *et al.*⁵ a laser beam was passed through a cell containing sodium dimers. The laser induces energy-conserving transitions between the bound vibrational-rotational states of the ground electronic state $X(^1\Sigma_g^+)$ and levels of the vibrational-rotational manifold of the excited electronic state $B(^1\Pi_u)$. If the laser induces a transition to a state above the B dissociation limit, the excited dimer dissociates producing excited free sodium atoms because of the very short lifetime for dissociation as compared to molecular fluorescent re-emission. The fluorescence intensity of the

free atoms is monitored as a function of laser frequency, providing a measure of the total transition probability to dissociative excited states. In order to interpret their data, for each laser frequency ω_i , Callender *et al.* set $I_i = |M(R_i)|^2 \times g(R_i)$, where $|M(R_i)|^2$ is the R -dependent electronic transition moment, $g(R_i)$ is a classically calculated factor, I_i is the measured atomic fluorescence intensity, and R_i , the internuclear separation, is determined by the equation

$$\epsilon_2(R_i) - \epsilon_1(R_i) = \hbar\omega_i. \quad (1)$$

Here ϵ_1 and ϵ_2 are the potential functions of the ground and excited electronic states, respectively. For each of eight argon-ion laser frequencies, associated with a specific internuclear separation as defined in Eq. (1), Callender *et al.*⁵ determined $|M(R_i)|^2$ from the ratio $I_i/g(R_i)$. Over the range of frequencies investigated (4579–5145 Å, corresponding to an internuclear separation range of 2.7–3.7 Å), they found that $|M(R_i)|^2$ varied by more than a factor of 4. Their intensity theory, however, was derived semiclassically; and in view of the potential advantages the technique offers, it seemed desirable to carry out the calculation with a standard quantum mechanical treatment in order to check the accuracy of the semiclassical result. We have performed such a calculation for molecular sodium and report the results in this paper.

From our calculation we find that, assuming a constant electronic transition moment, $|M(R)|^2$, our predicted intensities essentially agree with the experimental intensities reported by Callender *et al.*⁵ for all laser frequencies but 4579 Å. To allow a quantitative interpretation of this behavior we have used the r -centroid approximation to determine the functional dependence of $M(R)$. The accuracy of the $M(R)$ thus determined was tested by using it instead of a constant in the calculation of the intensities. The agreement between these calculated intensities and the experimental data was good. On this basis we may draw the following conclusions: (1) The r -centroid approximation when applied to induced atomic fluorescence spectra may serve as an accurate means of determining electronic transition moments; (2) within the experimental errors of the reported induced atomic fluorescence data for sodium, $|M(R)|^2$ has an essentially constant value over the range 2.9–3.7 Å and is nearly a factor of 2 larger than this value at 2.7 Å; and (3) the semiclassical theory used by Callender *et al.*⁵ does not accurately treat these fluores-

cence spectra.

Quantum mechanically, in the Born-Oppenheimer approximation, the total transition probability $I_{M(R)}$ is given within a constant factor by

$$I_{M(R)} = \sum_{v,J} |\langle v, J | M(R) | e(v, J, \omega_i) \rangle|^2 \times \exp(-E_{v,J}/kT) p_J \theta(E_{v,J} + \hbar\omega_i - D_J). \quad (2)$$

Here $|v, J\rangle$ is a bound vibrational-rotational eigenstate of the X electronic state with energy $E_{v,J}$; $|e(v, J, \omega_i)\rangle$ is a continuum state of the B electronic state with energy $E_{v,J} + \hbar\omega_i$; p_J is the Hönl-London intensity factor for rotational transitions; $\theta(E_{v,J} + \hbar\omega_i - D_J)$ is equal to 1 or 0 according as the transition does or does not reach the effective B dissociation energy, D_J . For $J = 0$, $D_J = \epsilon_2(\infty)$, but for $J > 0$ the excited-state potential function has, for large R , a local maximum⁶ equal to D_J . We are making the assumption that the quasibound excited states with energies below D_J and above $\epsilon_2(\infty)$ have negligible probability of dissociating and therefore do not produce any atomic fluorescence. Strictly speaking there is a local maximum in the potential even at $J = 0$ resulting from dipole-dipole resonance forces⁷ which would affect the low angular momentum states. However, predissociation by crossing to the $^1\Sigma_u$ state greatly diminishes the experimental consequences of these dipolar interactions in Na_2 and therefore we did not include them in our calculations. In addition, for simplicity we considered only the Q branch in our calculations. Although differences between P or R transitions and Q transitions are of importance in interpreting discrete spectra,⁸ for transitions terminating in continuum states they should scale together except for very low J . Similarly, effects of Λ -type doubling are not of importance.

In order to calculate $I_{M(R)}$ in Eq. (2), $M(R)$ was first taken to be a constant and removed from the summation so that Eq. (2) becomes

$$I_{M(R)=1} = \sum_{v,J} |\langle v, J | e(v, J, \omega_i) \rangle|^2 \times \exp(-E_{v,J}/kT) p_J \theta(E_{v,J} + \hbar\omega_i - D_J). \quad (3)$$

The relevant X and B eigenstates were calculated numerically using the Numerov method,⁹ and the overlap factors $\langle v, J | e(v, J, \omega_i) \rangle$ were also numerically calculated. The potential functions used for the calculations were taken from the turning-point data obtained from the Rydberg-Klein-Rees (RKR) analysis of Demtröder, McClintock, and Zare.⁹ Outside the range of their analysis (i.e., beyond $v = 23$ of the ground state and $v = 10$ of the excited state), the potential was extrapolated

with an $a + b/R^{12}$ function for small R , and a c/R^d function¹⁰ for large R .

It was found that rotational levels up to about $J = 180$ could be expected to contribute significantly to the intensity. To avoid recalculating the overlap factors for each of the 180 values of J which have significant population factors, the overlap factors were determined for a net of 34 values of J , roughly quadratically spaced over the range. Overlap factors for J values between the net points were determined by interpolation. Assuming the potential functions used are accurate, this interpolation procedure introduced the largest error in our calculation, which we estimate to be less than 10%.

In Fig. 1(a), we present the results of this calculation, using Eq. (3), and also show for comparison the experimental data of Callender *et al.*⁵ with their reported error estimates. The calculation was done for eight argon-ion laser frequencies and four additional frequencies as shown in the figure. The intensities are plotted in Fig. 1(a) versus the classical internuclear separations as determined with Eq. (1). The calculated intensities were normalized for the best fit with the experimental data and a smooth curve was drawn through the points. The comparison between our calculated curve and the experimental points⁵ is convincing evidence that for the seven laser frequencies in the range 4658–5145

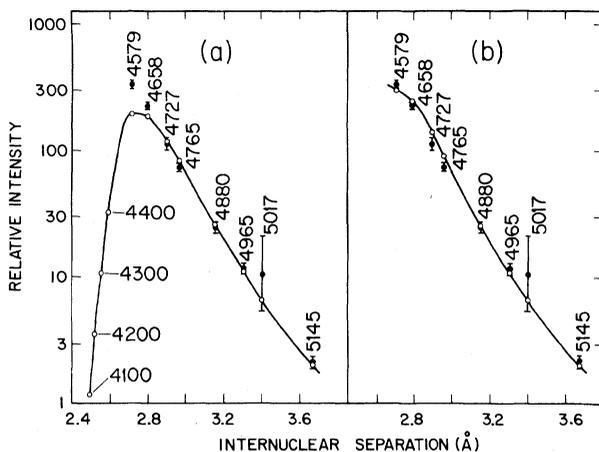


FIG. 1. Plot of laser-induced atomic fluorescence intensity as reported by Callender *et al.* (Ref. 5) (solid points) for each of the argon-ion laser frequencies. Abscissa is the internuclear separation as determined by either Eq. (1) or Eq. (5). (a) Theoretical curve evaluated for several incident frequencies (open circles) using Eq. (3). (b) Theoretical curve evaluated from Eq. (2) for each of the eight laser frequencies (open circles).

Å, the electronic transition moment $|M(R)|^2$ may be treated as a constant. This is in contrast to the variation of a factor of 3 over this range¹¹ reported by Callender *et al.*⁵ For cases in which errors of this magnitude are acceptable, the analysis of Callender *et al.*⁵ may be of use, but for a reliable determination of $|M(R)|^2$ a more accurate calculation, such as the one presented here, is required. It should be pointed out that although we would in general expect the semiclassical approach to agree with the quantum calculations, the disagreements here no doubt result from the approximation of Callender *et al.* that rotational angular momentum may be neglected.¹²

At incident wavelengths of 4579 Å and below, the quantum mechanically calculated intensity begins to fall off rapidly as a result of a strong variation in the Franck-Condon overlap factors. In order to check the effect on our own calculated intensities of the extrapolation used for the excited state potential, we recalculated these intensities using an $a + b/R^8$ extrapolation for small R . The resulting calculated fluorescence intensity curve was very similar to that obtained using the R^{-12} extrapolation, all points differing by less than 20%. It appears then that no reasonable modification of the assumed potential will significantly affect our calculated intensities and therefore the difference between our calculated point and the experimental point at 4579 Å is significant and represents a variation in the electronic transition moment.

To interpret quantitatively the difference between the calculated and the experimental point at 4579 Å we make use of the r -centroid approximation.¹³ In the approximation we may make the equality

$$\langle v' | M(R) | v'' \rangle = M(R_c) \langle v' | v'' \rangle, \quad (4)$$

where

$$R_c = \langle v' | R | v'' \rangle / \langle v' | v'' \rangle \quad (5)$$

and v' and v'' correspond to vibrational wave functions of different electronic states. Fraser¹³ has shown that within the r -centroid approximation, R_c , as defined in Eq. (5), may also be determined by Eq. (1) (i.e., $R_c = R_i$) and is, therefore, independent of the initial vibrational state. On this basis Eq. (2) may be rewritten

$$I_{M(R)=M(R_c)} = |M(R_c)|^2 \sum_{v,J} |\langle v, J | e(v, J, \omega_i) \rangle|^2 \times \exp(-E_{v,J}/kT) p_J \theta(E_{v,J} + \hbar\omega_i - D_J). \quad (6)$$

We see that the summation in the equation is

equal to the intensity we have calculated according to Eq. (3) under the assumption of constant $M(R)$, and have reported in Fig. 1(a). Thus the ratio of the previously calculated intensity to the experimentally measured intensity is proportional to $|M(R_c)|^2$, where R_c may be determined from either Eq. (5) or Eq. (1).

To determine the accuracy of our numerical calculations and of the r -centroid approximation, we numerically calculated matrix elements of R and R^2 . Except for a few cases in which the vibrational overlap factors were abnormally small we found a maximum error of $\pm 3\%$. As a result and from the relative insensitivity of our calculated intensities to the extrapolated potentials used, we conclude that the difference between the calculated and experimental point at 4579 Å may be properly interpreted as a factor of 1.7 ± 0.2 increase in the electronic transition moment at 2.72 Å over the value of the transition moment from 2.8 to 3.7 Å.

Although the preceding calculations indicate that our r -centroid approximation appears to be valid, clearly the definitive test of the validity of the approximation in this case may be made by calculating the fluorescence intensity numerically with Eq. (2) using an electronic transition amplitude $M(R)$ determined from the r -centroid analysis. We have evaluated $I_{M(R)}$ in this manner and present the results of the calculation in Fig. 1(b). The good agreement between the calculated curve and the experimental points in Fig. 1(b) demonstrates that the technique presented here is valid. The form of $M(R)$ used for this calculation¹⁴ is $M(R) = AR^2 + BR + C$ for $R \leq 2.9$ Å and $M(R) = 1$ for $R > 2.9$ Å. This function is shown in Fig. 2 (line) along with the r -centroid-determined

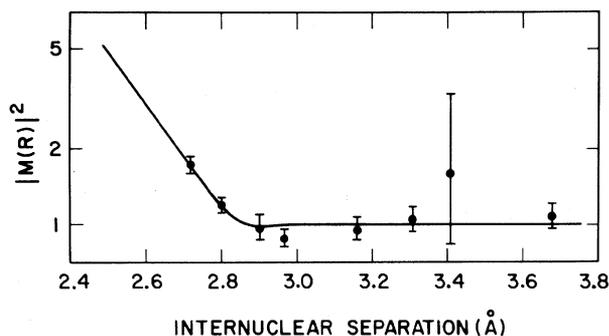


FIG. 2. Electronic transition moment $|M(R)|^2$ versus internuclear separation. The points correspond to the transition moment as determined from Eq. (3) and the data of Callender *et al.* (Ref. 5). The line is the functional form of $|M(R)|^2$ used to obtain Fig. 1(b).

values (points) used to obtain it. Although we have arbitrarily selected this functional form of $M(R)$, within the r -centroid approximation any function which passes through the points in Fig. 2 (e.g., an exponential) should also satisfy Eq. (2). More data in the 2.4–2.8-Å range (exciting wavelengths of 4000–4600 Å) would be desirable to determine more precisely the functional dependence of $|M(R)|^2$ in this region where it varies most rapidly.

Finally it should be pointed out that the use of Eq. (6) to determine electronic transition moments is superior to the standard r -centroid method when no more than a few vibrational progressions are used. When data from only a few vibrational progressions are available the calculated overlap factors are extremely sensitive to the precise form and position of the potential function. Scattering in the calculated transition moments determined from each vibrational progression often is accommodated by a least-squares fitting procedure using the overlap integral as a weighting factor.¹³ However, this is not necessary when data from atomic fluorescence can be analyzed with Eq. (6) since each datum point results from a sum of several individual transitions. We have shown that the total intensities calculated in this manner are relatively insensitive to the precise forms of the potential functions and we would expect therefore that this type of r -centroid treatment should be very useful in the accurate determination of electronic transition moments.

¹J. E. Hesser, *J. Chem. Phys.* **48**, 2518 (1968).

²P. F. Williams and D. L. Rousseau, *Phys. Rev. Lett.* **30**, 951 (1973).

³H. Klemsdal, *J. Quant. Spectrosc. Radiat. Transfer* **13**, 517 (1973).

⁴J. E. Gersten, *Phys. Rev. Lett.* **31**, 73 (1973).

⁵R. H. Callender, J. I. Gersten, R. W. Leigh, and J. L. Yang, *Phys. Rev. Lett.* **32**, 917 (1974).

⁶G. Herzberg, *Molecular Spectra and Molecular Structure: I. Spectra of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1950), p. 425f.

⁷G. W. King and J. H. Van Vleck, *Phys. Rev.* **55**, 1165 (1939).

⁸W. Demtröder, M. McClintock, and R. N. Zare, *J. Chem. Phys.* **51**, 5415 (1969).

⁹J. W. Cooley, *Math. Computation* **15**, 363 (1961).

¹⁰For the X state the values of a , b , c , and d used in the extrapolation were -4.84184×10^3 , 7.14301×10^7 , 1.84077×10^6 , and 4.40151 , respectively; and for the B state, -2.55981×10^3 , 3.50788×10^8 , 3.75730×10^6 , and 5.42419 , respectively. These values are for R ex-

pressed in angstroms and energy in inverse centimeters.

¹¹We have calculated the intensity from the semiclassical formula [Eq. (3) in Ref. 5] over the range 2.5–3.7 Å, and found some disagreement with the curve in Fig. 3(a) of Ref. 5. We attribute this difference to errors in the determination of $dr/d(\epsilon_2 - \epsilon_1)$. We have evaluated this derivative numerically from the RKR data of Ref. 8, extrapolated as discussed in the text, whereas Callender *et al.* (R. W. Leigh, private communication) utilized a less accurate method which involved approximating the RKR potentials with Morse potentials. A difference of up to a factor of 4 was found between the

quantum curve calculated from our Eq. (3) and the semiclassical intensity curve determined with the RKR data.

¹²Recently Callender *et al.* [R. H. Callender, J. I. Gersten, R. W. Leigh, and J. L. Yang, Phys. Rev. Lett. **33**, 1311(C) (1974)] incorporated angular momentum in their semiclassical theory and obtained a result in qualitative agreement with our quantum calculation.

¹³P. A. Fraser, Can. J. Phys. **32**, 515 (1954).

¹⁴For R expressed in angstroms, the values used for A , B , and C are 24.64, -142.52, and 207.02, respectively.

Comments on a New Scaling Hypothesis in High-Energy Collisions*

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Dao *et al.* have demonstrated that single-particle distributions in inclusive reactions scale in a new variable. We comment on the nature of the scaling relation satisfied and note that their parametrization of the single-particle distributions requires only two parameters rather than the six they used.

A recent paper by Dao *et al.*¹ begins with the sentences, "The scaling behavior of a distribution $f(x_1, x_2)$ with independent variables x_1 and x_2 can be defined in terms of a homogeneous equation,

$$f(\lambda_1 x_1, \lambda_2 x_2) = \lambda f(x_1, x_2). \quad (1)$$

The distribution f scales if there exist scaling parameters λ_1 , λ_2 , and λ for which Eq. (1) is satisfied."² The authors then make the hypothesis that single-particle distributions in inclusive reactions satisfy Eq. (1). It becomes apparent on further reading of the paper that the authors do not intend $f(\lambda_1 x_1, \lambda_2 x_2)$ to be the same function of its argument as $f(x_1, x_2)$ is of its argument. Rather, the authors mean that a given function of three variables $f(x_1, x_2, s)$ scales if there exists a function of two variables $g(x_1, x_2)$ such that

$$g(\lambda_1 x_1, \lambda_2 x_2) = \lambda f(x_1, x_2, s), \quad (2)$$

where λ_1 , λ_2 , and λ are functions of s alone. It is the presence of the third variable s which makes Eq. (2) nontrivial.

The authors give as examples the single-particle distributions in transverse (p_T) and longitudinal (p_L) momentum variables, with

$$\begin{aligned} \lambda(s) &= \langle p_T \rangle \langle p_L \rangle, & \lambda_1(s) &= 1/\langle p_T \rangle, \\ & & \lambda_2(s) &= 1/\langle p_L \rangle, \end{aligned} \quad (3)$$

and s standing for the square of the energy in the

c.m. system. The authors test Eq. (2) after a single integration over p_T or p_L , obtaining the following relations for the inclusive cross sections $d\sigma/dp_T$ and $d\sigma/dp_L$:

$$\langle \langle p_T \rangle / \sigma \rangle d\sigma/dp_T = \varphi_T(p_T/\langle p_T \rangle), \quad (4)$$

$$\langle \langle p_L \rangle / \sigma \rangle d\sigma/dp_L = \varphi_L(p_L/\langle p_L \rangle). \quad (5)$$

The functions appearing in Eqs. (4) and (5) are related to the f and g of Eq. (2) by³

$$\sigma^{-1} d\sigma/dp_i = \int f(p_T, p_L, s) dp_j, \quad (6)$$

$$\varphi_i \left(\frac{p_i}{\langle p_i \rangle} \right) = \int g \left(\frac{p_T}{\langle p_T \rangle}, \frac{p_L}{\langle p_L \rangle} \right) \frac{dp_j}{\langle p_j \rangle}, \quad (7)$$

where the subscripts i, j stand for either T or L and $i \neq j$. Equations (4) and (5) are conventional scaling equations in the new variables $p_i/\langle p_i \rangle$.

The authors have shown the important result that, in a rather large energy range, the existing data on inclusive cross sections satisfy Eqs. (4) and (5) to a good approximation. They have also shown that the functions φ_i can be well approximated by the simple forms

$$\varphi_T \left(\frac{p_T}{\langle p_T \rangle} \right) = a \left(\frac{p_T}{\langle p_T \rangle} \right)^c \exp \left[-b \left(\frac{p_T}{\langle p_T \rangle} \right) \right], \quad (8)$$

$$\varphi_L \left(\frac{p_L}{\langle p_L \rangle} \right) = d \exp \left[-e \frac{p_L}{\langle p_L \rangle} - f \left(\frac{p_L}{\langle p_L \rangle} \right)^2 \right], \quad (9)$$

where a , b , c , d , e , and f are parameters which