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Transition Dipole Moment of Na_2 and Its Variation with Internuclear Distance*

M. M. Hessel, E. W. Smith, and R. E. Drullinger
Division 277, National Bureau of Standards, Boulder, Colorado 80302
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The electronic transition dipole moment was determined for the transition $X^1\Sigma_g^+ \leftarrow B^1\Pi_u$ of Na_2 and was found to be $6.8 + 0.5r$ D over a range of internuclear distance r of 2.6–5.0 Å. Our results agree with earlier lifetime measurements and are in qualitative agreement with semiquantitative theoretical calculations, but they strongly disagree with the recent work of Callender, Gersten, Leigh, and Yang.

We have measured the intensities of fluorescent series produced by laser excitation from the $X^1\Sigma_g^+$ ground state to a specific vibrational and rotational level (v', J') of the $B^1\Pi_u$ excited state of Na_2 . Using these intensities, Franck-Condon factors, r centroids, and r^2 centroids we have determined the variation of electronic transition moment with internuclear distance. To obtain an absolute value of the electronic transition moment we used the lifetime measurements of Baumgartner, Demtroder, and Stock.¹ For both the lifetime measurements and intensity measurements we find that the transition moment *increases* by about 30% with increasing r from 2.6 to 5.0 Å. These results are in qualitative agreement with the calculations of Tango and Zare,² but strongly disagree with those of Callender *et al.*³ who find a 400% *decrease* in transition moment for a smaller range of internuclear distance, 2.7–3.7 Å.

The Einstein coefficient A for the radiative transition $^1\Sigma_g^+ v'' J'' \leftarrow ^1\Pi_u v' J'$ (at frequency $\nu_{v'v''}$) can be written in the form

$$A(^1\Pi_u v' J'; ^1\Sigma_g^+ v'' J'') = (4/3\hbar)(2\pi\nu_{v'v''})^3 [S(J', J'')/(2J'' + 1)] |\langle v' | R | v'' \rangle|^2, \quad (1)$$

where S is the rotational line strength or Honl-London factor and $\langle v' | R | v'' \rangle$ denotes the vibrational matrix elements of the electronic transition dipole operator $R(r)$. We will assume that the dependence of R on internuclear separation r can be expressed in terms of a power series,⁴ $R(r) = R_0 + \alpha r + \beta r^2 + \dots$, so that

$$\langle v' | R | v'' \rangle = \langle v' | v'' \rangle (R_0 + \alpha \langle v' | r | v'' \rangle / \langle v' | v'' \rangle + \beta \langle v' | r^2 | v'' \rangle / \langle v' | v'' \rangle + \dots). \quad (2)$$

The simplest approximation to $R(r)$ is obtained by assuming that it does not change with r ; hence $R(r) \approx R_0$ and one needs only the Franck-Condon factors $q_{v'v''} = \langle v' | v'' \rangle^2$. Another approximation, the r -centroid method,⁴ assumes that

$$\langle v' | r^n | v'' \rangle / \langle v' | v'' \rangle = (\langle v' | r | v'' \rangle / \langle v' | v'' \rangle)^n, \quad (3)$$

for all powers of r required in Eq. (2). For all transitions which we have considered we find $\beta \approx 0$ and hence the r -centroid approximation would have been sufficient; however, there is no *a priori* way to know this and so we used a second-order expansion of $R(r)$. Our calculation therefore requires a knowledge of the Franck-Condon factors, $q_{v'v''}$; the r centroid, $r_{v'v''}^c \equiv \langle v' | r | v'' \rangle / \langle v' | v'' \rangle$; and the r^2 centroid,

$r_{v',v''}{}^{2c} \equiv \langle v' | r^2 | v'' \rangle / \langle v' | v'' \rangle$; these quantities were all determined from vibrational wave functions based on Rydberg-Klein-Rees potentials.⁵

The expansion coefficients R_0 , α , and β can be determined by substituting Eq. (2) into Eq. (1) and using

$$\tau_{v'}^{-1} = \sum_{v'' J''} A(v' J', v'' J'') = \frac{4}{3} [(2\pi)^3 / \hbar] \sum_{v''} \nu_{v',v''}{}^3 q_{v',v''} (R_0 + \alpha r_{v',v''}{}^c + \beta r_{v',v''}{}^{2c})^2, \quad (4)$$

for radiative lifetime measurements and

$$I(v', v'') \propto \nu_{v',v''}{}^3 q_{v',v''} |R_0 + \alpha r_{v',v''}{}^c + \beta r_{v',v''}{}^{2c}|^2 \quad (5)$$

for measurements of fluorescence line intensities. In both cases the coefficients R_0 , α , and β were determined by a least-squares fit to the experimentally observed lifetimes, $\tau_{v'}$, and intensities, $I(v', v'')$. The lifetime data were obtained from Baumgartner, Demtroder, and Stock, and the fluorescent line intensities were determined by experiments which we performed for this purpose and which will be discussed later. The latter have the disadvantage that R_0 cannot be determined uniquely because absolute intensity measurements were not made; we therefore used the value of R_0 determined from the lifetime measurements when analyzing our line-intensity data.

Table I reproduces the lifetime data of Baumgartner, Demtroder, and Stock along with a few of the sums needed for the calculation; the sum over vibrational states v'' was truncated at a value such that $\sum_{v''} q_{v',v''} \geq 0.99$ in order to insure that enough states were used. The values of R_0 , α , and β obtained by a least-squares fit are $R_0 = 6.8 \pm 0.2$ D; $\alpha = 0.4 \pm 0.1$ D/Å; $\beta < \alpha/10$ D/Å².

The coefficients α and β were also determined from a measurement of the intensities of fluorescent lines which were excited by the 4880-Å and 4765-Å lines of an Ar⁺ laser. The sodium was contained in the cell and oven described by Drullinger and Zare.⁷ The cell was at a temperature of 207°C corresponding to a sodium vapor pres-

sure of 2.5×10^{-4} Torr (1 Torr = 133.3 N/m²). The molecular fluorescence was observed at right angles to the incoming laser beam and the intensity of the various fluorescence lines was measured by means of a $\frac{1}{3}$ -m scanning spectrometer. A commercial spectral irradiance lamp⁸ was used to calibrate the spectrometer-photomultiplier combination so that a photon-intensity calibration (relative quantum efficiency) accurate to about 3% was obtained for the wavelength region of interest. The detected fluorescence was unpolarized because the fluorescence observations were made along the plane of the laser polarization vector. The spectrometer was scanned from 4600 to 5400 Å and the signal from the photomultiplier was converted to a frequency, stored digitally every 0.25 Å in a multichannel analyzer, and recorded on magnetic tape. Figures 1(a) and 1(b) show the calibrated spectrometer scans for the 4880-Å and 4765-Å laser excitation of Na₂. The intensities are all relative (in terms of photons per second per square centimeter) and corrected for photomultiplier and spectrometer response. The 4880-Å laser line produces⁹ a strong ($v' = 6, J' = 43$) → ($v'' = 43$) and a weak ($v' = 10, J' = 42$) → ($v'' = 41$ and 43) fluorescence series, whereas the 4765-Å line produces the ($v' = 10, J' = 12$) → ($v'' = 11$ and 13) and ($v' = 6, J' = 27$)

TABLE I. Data for the $B^1\Pi \rightarrow X^1\Sigma$ transitions of Na₂.

λ_{exc} (Å)	v'	J'	v''	J''	τ^c (nsec)	v_{max}''	$\sum_{v''=0}^{v_{max}''} q_{v',v''}{}^b$	$\sum_{v''} \rho^b$	$\sum_{v''} \rho r^c{}^b$	$\sum_{v''} \rho r^{2c}{}^b$
4579 ^a	27	31	7	31	7.12	43	0.991	6.67	135	29.2
4658	17	37	4	38	7.00	43	0.999	6.64	135	29.2
4727	9	38	1	37	6.72	22	0.999	7.53	100	27.2
4765	10	12	3	13	6.65	22	0.998	7.52	100	27.2
4880	6	43	3	43	6.50	23	0.999	7.62	97.8	27.1

^aIdentification of this line from Ref. 6.

^bThese were obtained from the molecular constants of Ref. 6, and computer codes of Albritton *et al.* (Ref. 5). $\rho = 10^{12} \nu_{v',v''}{}^3 q_{v',v''}$; ν is in units of cm⁻¹, r^c in Å, and r^{2c} in Å².

^cFrom Ref. 1.

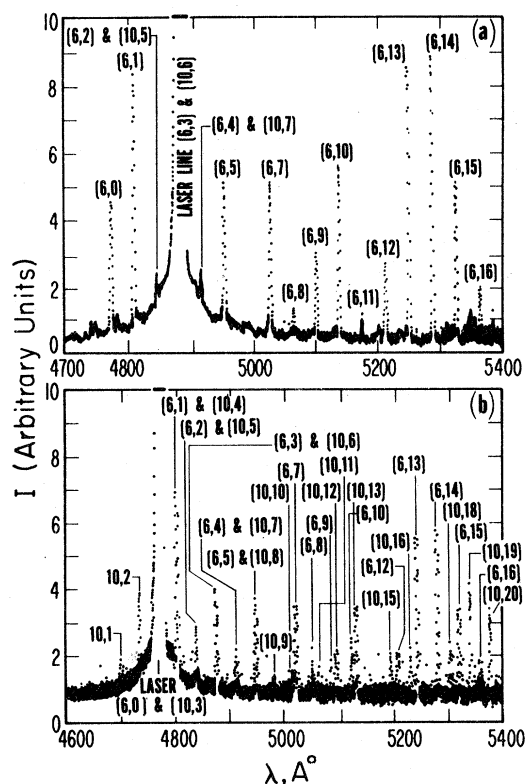


FIG. 1. (a) Fluorescence series ($v' = 6, J' = 42$) \rightarrow ($v'', J'' = 43$) excited by the 4880-Å laser line. Weak ($v' = 10, J' = 42$) series also observed. (b) Fluorescent series ($v' = 10, J' = 12$) \rightarrow ($v'', J'' = 11$ and 13) and ($v' = 6, J' = 27$) \rightarrow ($v'', J'' = 26$ and 28) excited by the 4765-Å laser line.

\rightarrow ($v'', J'' = 26$ and 28) series. Since the vapor pressure is $< 10^{-3}$ Torr no collisionally transferred lines could be observed and collisional effects could be neglected. For each of the laser lines six independent scans were made, three at slit widths corresponding to a 5-Å linewidth and three at a 2-Å linewidth. The line profiles were triangular and the peak values were used to obtain line intensities. The measurements and the calculated values of $q_{v',v''}$, r^c , and r^{2c} are given in Table II. With the use of $R_0 = 6.8$ D in Eq. (5) a least-squares fit gave $\alpha = 0.5 \pm 0.2$ D/Å and $\beta < \alpha/10$, in excellent agreement with the lifetime measurements.

It is important to note that three independent sets of data (i.e., lifetime data and the $v' = 6$ and $v' = 10$ fluorescence series) all gave the same values for α and β . This justifies the series expansion, Eq. (2), for the range of r considered and it gives one confidence in the quoted value of α . Further, since $\beta \approx 0$, the r -centroid approxima-

TABLE II. Typical data for the ($v' = 6, J' = 43$) \rightarrow ($v'', J'' = 43$) transitions of Na_2 .

v''	I(a)	I(b)	$q_{v',v''}$	$r_{\text{Å}}^c$	$r_{\text{Å}}^{2c}$	$\nu_{\text{cm}^{-1}}$
0	1.34	1.39	.058	2.97	8.80	20950
1	1.39	1.32	.120	3.03	9.20	20794
2	(c)	(c)	.007	3.11	9.75	20640
3	laser	laser	.070	3.16	9.98	20487
4	(c)	(c)	.012	3.24	10.57	20335
5	1.53	1.47	.067	3.29	10.83	20185
6	(d)	(d)	.002	---	---	---
7	1.43	1.43	.075	3.43	11.80	19889
8	1.65	1.55	.013	3.48	12.04	19744
9	1.48	1.37	.040	3.59	12.94	19600
10	1.42	1.47	.084	3.65	13.35	19458
11	(c)	(c)	.008	3.69	13.55	19312
12	1.58	1.50	.039	3.85	14.85	19178
13	1.57	1.60	.140	3.92	15.38	19041
14	1.63	1.54	.146	4.01	16.70	18905
15	1.66	1.66	.081	4.10	16.86	18771
16	1.67	1.53	.028	4.22	17.74	18639
17	(d)	(d)	.007	---	---	---

^a $I(a) = I/\nu^3 q_{v',v''}$ (arbitrary units), 5 Å width.

^b $I(b) = I/\nu^3 q_{v',v''}$ (arbitrary units), 2 Å width.

^cThese lines are overlapped by the (10,42) series.

^dNot observed.

tion is valid and we may use the idea that the radiative transition $v' \rightarrow v''$ "takes place" at the internuclear distance $r_{v',v''}^c$; we may therefore infer that our results are valid in the range $2.6 \text{ Å} \leq r \leq 5.0 \text{ Å}$.

Tango and Zare² have calculated the transition moment as a function of internuclear distance using simple Coulomb wave functions with a quantum defect parameter $n^* = 2$. In Fig. 2 we compare our results with these calculations and with the results of Callender *et al.* We have plotted

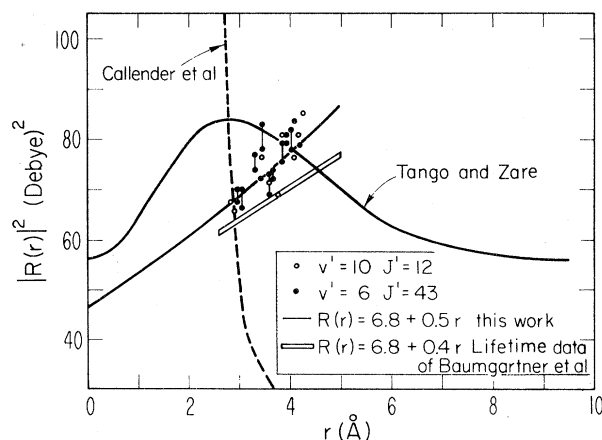


FIG. 2. Transition moment versus internuclear separation.

Tango and Zare's dipole strength ($\frac{1}{3}$ of their $|\langle \Pi | R | \Sigma \rangle|^2$) versus r ; the $|R(r)|^2$ scale of Callender *et al.* is arbitrary and we have chosen a scale factor which keeps their data on the graph. In comparing our results with those of Tango and Zare it should be noted that they used $n^* = 2$ only for simplicity. An "exact Coulomb" calculation¹⁰ using $n^* = 2.1$ would change the radial scaling and reduce the $r \rightarrow 0$ and $r \rightarrow \infty$ asymptotes slightly (see p. 81 of Ref. 10).

The results of Callender *et al.* disagree strongly with our results and those of Tango and Zare. It is unclear at what point the theory or experiment of Callender *et al.* is inadequate. Their use of a two-state model for a molecular transition neglects the dependence of $\langle v' | R | v'' \rangle$ on vibrational wave functions but this may not be serious since the vibrational spacing $\omega_e \sim 150 \text{ cm}^{-1}$ is smaller than $kT \sim 430 \text{ cm}^{-1}$ and the vibrational structure may be negligible. They also assumed that all molecules having an energy greater than that of the atomic p state, $\epsilon_2(\infty)$, will dissociate and produce atomic fluorescence; this assumption neglects both the electronic potential barrier¹¹ and the rotational energy barrier which exist at large r and which can prevent dissociation. There may also be experimental uncertainties associated with radiation trapping, etc.

In summary, we find a 30% variation in the transition moment over the range 2.6–5.0 Å. We find that the r -centroid technique is valid over this range of r and that three independent measurements give the same value for the relative r dependence, α . The absolute value of $R(r)$ was determined from the lifetime data of Baumgartner, Demtroder, and Stock and the resulting $|R(r)|^2$ agrees qualitatively with the calculations

of Tango and Zare but disagrees strongly with the results of Callender *et al.*

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Velocity Selection by Doppler Shift: A General Method for Studying Excited-State Collisions*

William D. Phillips and David Pritchard

*Physics Department and Research Laboratory of Electronics,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

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We show that the Doppler shift can provide velocity resolution in excited-state molecular-collision experiments which is comparable to that obtainable in molecular-beam machines. In addition, the state of the quasimolecule formed in the collision can be selected.

Excited-state atomic and molecular collision processes such as excitation transfer,¹ fine-structure-changing collisions,² electronic-to-vibrational energy transfer,^{3,4} and rotational energy transfer⁵ have long been studied with the use of spectral lamps, resonance lamps, and more recently gas lasers as