Electronic transition moment variation and Einstein coefficients for the NO($B^2\Pi - X^2\Pi$) system

Lawrence G. Piper,^{a)} Thomas R. Tucker,^{b)} and William P. Cummings^{c)} Physical Sciences Inc., 20 New England Business Center, Andover, Massachusetts 01810

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This paper details an investigation of the variation in the electronic transition moment with internuclear separation for the NO($B^2\Pi - X^2\Pi$) transition. Measurements of the relative intensities of a number of NO B-X vibronic transitions having a common upper level were used to construct a relative transition-moment function between 1.27 and 1.60 Å. After normalizing this relative function by experimentally determined radiative lifetimes, the transition-moment function was extended down to 1.23 Å by incorporating data from oscillator strength measurements. In contrast to empirical transition-moment functions that have been proposed previously, the function in this paper decreases with increasing internuclear separation. Unlike these other functions, however, this one is consistent with theoretical predictions, with most available oscillator strength data, and with the observed trend in *B*-state radiative lifetimes as a function of vibrational level.

I. INTRODUCTION

The NO($B^2\Pi - X^2\Pi$) system gives rise to the wellknown β bands of NO. These bands are prominent in air and nitric oxide discharges and are excited in a number of chemiluminescent processes, most notably the three-body recombination of oxygen and nitrogen atoms. Surprisingly, the quantitative spectroscopic aspects of this system have not been well characterized.

Robinson and Nicholls¹ reported that the electronic transition moment, $R_e(r)$, of the NO(B-X) system increased linearly with increasing internuclear separation. They based their conclusions upon observations of relative intensities of a number of NO β bands that had common upper vibrational levels. Thirty years later, using a similar experimental approach and analysis, Vilesov and Matveev² determined a transition-moment function that was almost identical to that of Robinson and Nicholls. In the interim, Kuz'menko et al.3 derived a substantially different electronic transition moment function, but one that also increased with increasing internuclear separation, although much more strongly than the other two functions. They relied on absorption oscillator strength measurements for small values of internuclear separation and absolute emission measurements derived from shock-tube experiments for large values of internuclear separation.

All three of these transition-moment functions predict that the radiative lifetimes of the NO *B* state vibrational levels will increase with increasing vibrational level. Such a trend is contrary to all published experimental measurements⁴⁻⁶ which show clearly that the lifetimes of the higher vibrational levels are shorter than those of the lower levels. Furthermore, if the two linear transition-moment functions are normalized so as to yield a radiative lifetime of 2.0 μ s for v' = 0 as given by the recent measurement of Gadd and Slanger,⁶ they underpredict the absorption oscillator strengths for the 0–0 through 6–0 transitions by more than a factor of two compared to all available experimental data.⁷⁻⁹ Kuz'menko *et al.*'s transition-moment function predicts radiative lifetimes for NO(*B*) which are even more discordant with available experimental measurements than the other two empirical functions.

In contrast to the experimentally based transition-moment functions, the results from three *ab initio* calculations¹⁰⁻¹² indicate that the electronic transition moment of the NO(*B*-*X*) system decreases with increasing internuclear separation. Cooper's¹⁰ *ab initio* function falls very rapidly, dropping a factor of 2 between 1.22 and 1.3 Å. The decrease in $R_e(r)$ then moderates somewhat, dropping another factor of 2 between 1.3 and 1.5 Å. de Vivie and Peyerimhoff's function,¹¹ on the other hand, is essentially linear, dropping roughly a factor of 2 between 1.3 and 1.6 Å. Langhoff *et al.* have proposed a function that combines a steep drop in the transition moment function at small r (almost a factor of 2 between 1.20 and 1.27 Å) with a much more moderate decline at larger r (about a third between 1.30 and 1.60 Å).

The plethora of inconsistent results has led us to reinvestigate the NO(B-X) system. We use a branching-ratio technique to determine the relative variation in the electronic transition moment with internuclear separation. This allows us to normalize our relative data to the radiative lifetime measurements of Gadd and Slanger. We then extend our function to shorter internuclear distances by incorporating $R_e(r)$ values determined from oscillator-strength measurements.^{7,8}

Our transition moment function has a slope opposite that proposed by all three previous experimentally derived functions, but in accord with *ab initio* calculations. Our function is consistent, furthermore, with most available absorption oscillator strength and radiative lifetime measurements.

[&]quot;Author to whom correspondence should be addressed.

[&]quot;Mailing address: 550 S. Ruston, Evansville, IN 47714.

^{c)} Current address: Dept. of Physics, University of Georgia, Athens, Georgia.

II. EXPERIMENT

The NO- β bands were excited in a discharge-flow apparatus from the recombination of O and N atoms in argon.¹³ A microwave discharge through a flow of nitrous oxide in argon produced the atoms.¹⁴ The mole fraction of N₂ O was kept low (less than 1%) in order to avoid production of NO in the discharge. The NO destroys the N atoms quite efficiently.¹⁵

Spectra were recorded between 200 and 530 nm at moderate resolution ($\Delta \lambda \approx 0.25$ nm) using a 0.5 m scanning monochromator that was equipped with a thermoelectrically cooled photomultiplier and a photon-counting rate meter. A computer-based data acquisition system digitized the output of the photon counter and stored the data for subsequent analysis. Figure 1 displays a portion of one of the spectra recorded for this study. Bands from all seven of the vibrational levels of NO(B) that are below the predissociation limit, i.e., v' = 0-6, radiate over the spectral range studied, 200 to 530 nm. Relative populations of the emitting levels vary with pressure and with the third body. They are more relaxed at higher buffer gas pressures and also more relaxed in nitrogen than in argon. In 2.5 torr of argon, the relative populations of v'=0to 6, respectively, are 100:14:20:30:11:7:8.

The variation in the response of the detection system as a function of wavelength was determined by resolving the output of standard quartz-halogen and deuterium lamps. A BaSO₄ screen reflected the lamp emission into the monochromator, thereby ensuring that the optics were filled. The small drop in the reflectivity of the screen at shorter wavelengths was included in the response function calculations.^{16,17} Calibrations obtained from the two lamps agreed excellently in the region of spectral overlap, 300 to 400 nm. The only optical element between the flow reactor and the entrance slit of the monochromator was a CaF₂ window which transmits uniformly over the relevant spectral region. This procedure ensured that the relative response determined from the lamps would not be modified by the presence



FIG. 1. The chemiluminescence spectrum generated from the recombination of O and N atoms in argon between 230 and 400 nm.

of other optical elements, such as a collection lens or even a curved flow reactor wall.

Spectral analysis involved dividing each spectrum into a number of discrete segments. Each segment contained only one transition from each of the seven upper levels of NO(B). These segments were then fit by computer to determine the intensities of each of the bands in the spectral segment. This spectral-fitting procedure allows intensities to be determined unambiguously in cases of partial overlap between bands. In a few cases the overlap was so great that reliable intensities could not be determined. Such bands were not included in the analysis. Figure 2 shows one of the spectral segments along with its associated synthetic fit. Without the spectral fitting analysis, we would have been unable to determine the intensities of any of the bands in this spectral region except that of the 2,16 band.

We have described our spectral-fitting procedure in some detail previously.^{18,19} A least-squares-fitting routine adjusts the populations of each vibrational level in a computer generated synthetic spectrum of the NO- β bands so as to match best the experimentally determined spectrum. We used spectral constants tabulated in Huber and Herzberg²⁰ to calculate the synthetic spectrum. Incorporating the variation in the spin–orbit coupling constant with vibrational level was imperative to obtaining adequate fits.

III. RESULTS

A. Fit to branching-ratio measurements

The intensity of emission from a given band is the product of the number density in the upper state, $N_{v'}$, and the Einstein coefficient for spontaneous radiation, $A_{v'v'}$. Generally, one can separate the Einstein coefficient into a product of several factors²¹ including the Franck–Condon factor, $q_{v'v'}$, the cube of the transition frequency, $v_{v'v'}$, and the square of the electronic transition moment, $R_e(r)$. This latter quantity is a function of the internuclear separation, r. The internuclear separation appropriate to a given transition is known as the the r centroid of that transition, $\overline{r}_{u'v'}$. Thus,

$$I_{v'v''} = N_{v'}A_{v'v'} = \kappa N_{v'}q_{v'v'}v_{o'v'}^{*}$$

$$\times \frac{(2-\delta_{0,\Lambda'+\Lambda'})}{(2-\delta_{0,\Lambda'})}R_{e}^{2}(\bar{r}_{v'v'}), \quad (1)$$



FIG. 2. A portion of the NO($B^2\Pi - X^2\Pi$) spectrum excited by the recombination of O with N in argon. The light line represents the data while the heavy line is the best-fit synthetic spectrum. The band heads are marked for each band (v',v'').

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where κ is a constant ($\kappa = 64\pi^4/3h$ for ν in cm⁻¹), and the subscripts, Λ , on the Kronecker delta characterize the orbital angular momentum of the electronic states. This definition of the Einstein coefficient²² is consistent with the recommendations of Whiting *et al.*²³

The reduced intensities of bands in a progression having a common upper level,

$$\frac{I_{v'v^*}}{q_{v'v^*} \gamma_{v'v^*}^3} = \kappa N_{v'} R_e^2(\bar{r}_{v'v^*}), \qquad (2)$$

are a function only of the electronic-transition moment. The square root of the ratios of these reduced intensities to that of a single band in the progression vary from one another, therefore, in the same way that the electronic transition moment varies with internuclear separation. The conditions under which this analysis is valid have been documented extensively in the literature over the past 35 years.^{21,24-27} Although the *r*-centroid approximation is only strictly valid when $R_e(r)$ is a linear function, Fraser²⁰ and McCallum²⁴ have shown that the *r*-centroid approximation describes the electronic transition moment function quite well for most molecules even when higher-order polynomial or exponential functions are used to model $R_e(r)$.

We calculated the reduced intensities using the band intensities determined from the spectral fitting procedure described above and the Franck-Condon factors and band origins calculated by Albritton et al.28 The r centroids needed for the analysis also derive from Albritton et al.'s calculations. These Franck-Condon factors are based on a Rydberg-Klein-Rees (RKR) potential and agree to better than 10 percent with the RKR based Franck-Condon factors of Jain and Sahni.²⁹ The Morse potential based Franck-Condon factors of Nicholls³⁰ and Ory et al.³¹ agree with those of Albritton et al. to better than 20 percent for Franck-Condon factors $\gtrsim 0.02$. Sizeable disagreements occur for smaller Franck-Condon factors, but such bands contribute negligibly to the observed intensities. In general, RKR-based Franck-Condon factors tend to be more accurate than those that use Morse potential functions in their calculation.

Figure 3 shows data for bands originating from levels v' = 0-3 plotted together. Transitions used in the fit included the following: v' = 0, v'' = 2-15; v' = 1, v'' = 3-7, 10–16; v' = 2, v'' = 2-5, 8–16; and v' = 3, v'' = 1-5, 7, 8, 11, 12, and 15–18. The line through the data is a least-squares-fit to the function

$$R_{e}(\bar{r}_{v'v^{*}})|_{rel} = 1.40 - 0.40\bar{r}_{v'v^{*}} + 1.508 \times 10^{5} \exp(-10.07 \,\bar{r}_{v'v^{*}}).$$
(3)

A least-squares routine adjusted the normalization factor for each progression to minimize the difference between the data for each progression and the function describing the variation with *r* centroid for all progressions. The procedure was to fit just one progression initially and then adjust the normalization factors for each of the other progressions so that they would match, as closely as possible, this initial fit. The criterion for the fitting procedure was minimization of the sum of the squares of the differences between the analytical function and the individual data points (the residuals). All of the adjusted data then were refit to determine a new



FIG. 3. Relative variation in the transition moment for the NO($B^2\Pi - X^2\Pi$) system as a function of internuclear separation.

best-fit function. The individual progressions then were readjusted to reduce further the sum of the squares of the residuals. After several iterations, no further improvements in the fit could be realized. The variance of the final fit indicated that the function reproduced the data to within about 5%.

The data could be fit just as well to a quadratic function or to an exponential function that didn't have a linear term in $\bar{r}_{\nu'\nu'}$. A quadratic polynomial fit to our data goes through a minimum at $\bar{r} \sim 1.55$ A and then increase at larger \bar{r} . This is physically unreasonable since R_e must vanish at large internuclear separations. A simple exponential function also is physically unreasonable because it becomes constant at large r. The exponential function with the linear term, on the other hand, decreases in value throughout the range of internuclear separation that is important for determining Einstein coefficients.

We used Gadd and Slanger's radiative lifetime values for v' = 0-3 to place our relative transition-moment function on an absolute basis. The reason for restricting the normalization procedure to vibrational levels three and below is that our data provide a transition-moment function that is valid only over the range 1.27 Å $\leq r \leq 1.60$ Å. This range encompasses well over 90% of the important vibronic transitions from v' = 0-3, whereas more than 40% of important transitions from v' = 4-6 occur outside this range.

The inverse of the radiative lifetime is given by

$$\tau_{v'}^{-1} = \zeta \sum_{v'} q_{v'v'} v_{v'v'}^3 |R_e(\bar{r}_{v'v'})|_{\rm rel}^2, \tag{4}$$

where the scaling factor, ζ , is chosen so that τ in Eq. (4) gives the experimentally determined value. The average scal-

ing factor determined from Eq. (4) gives calculated radiative lifetimes for v' = 0-3 that agree with Gadd and Slanger's experimental values to within $\pm 4\%$.

B. Limits of validity of branching ratio fit

Equation (3) is a reasonably good representation of our data over the range of its validity, 1.27 to 1.60 Å. The least-squares-fit indicates an overall uncertainty of about 5%. Extrapolation of our function outside this region could lead to problems, however (*vide infra*). Most important transitions from v' = 0-3 occur within this range of internuclear separations, so that determining the lifetimes and Einstein coefficients of transitions involving these levels should not be subject to serious extrapolation error.

For the higher vibrational levels, the sum of the Franck– Condon factors for transitions from a given upper level to all lower levels is somewhat smaller than the value of unity that is required by quantum mechanical sum rules. This indicates that our sum over Einstein coefficients could be incomplete, and that if a greater range of lower levels were included in the summation, the radiative lifetime might be even smaller than those we calculate using our transition-moment function.

Any errors in radiative lifetime introduced by the incomplete summation, however, will be small because the missing transitions occur at longer wavelengths. The v^3 factor in Eq. (1) is sufficiently small at these longer wavelengths that transition probabilities will be small even for transitions with sizable Franck-Condon factors. For example, if we assumed that the Franck-Condon factor for the 6,20 band were 0.423, i.e.,

$$1 - \sum_{v^* = 0}^{19} q_{6v^*},$$

the resulting Einstein coefficient would add less than 4% to the total radiative decay rate of v' = 6. In reality, the sum of the Franck–Condon factors for the 6,21 and 6,22 bands is only 0.27,³² so that the uncertainty arising from the incomplete set of Franck–Condon factors is somewhat less than 4%.

A more serious problem is that our transition momentfunction by itself probably underpredicts values at the smaller internuclear separations. Mixing between the *B* and *C* states becomes important at an internuclear separation around 1.25 Å.¹² This mixing causes a fairly abrupt change in slope of the transition-moment function. The increase in R_e values with decreasing internuclear separation becomes much more rapid below 1.25 Å that it was above 1.25 Å. Since our experimental data provide a transition-moment function that is valid only down to 1.27 Å, using our function to calculate Einstein coefficients for transitions at smaller internuclear separations may result in values that are too small and will predict radiative lifetimes that are somewhat too long.

The vibrational levels that would be most affected by an extrapolation error are the higher ones, v' = 4-6, and only for sequences $\Delta v = 6$ through $\Delta v = 2$. Our function should provide reasonably accurate Einstein coefficients for all important transitions from the other vibrational levels, as well

as for those transitions from the higher vibrational levels occurring in sequences smaller than $\Delta v \ge 2$.

C. Extension of transition-moment function

In order to reduce extrapolation errors associated with our function, we extended it to smaller internuclear distances by including results from oscillator-strength measurements. The oscillator strength, $f_{v'v^*}$, is determined from absorption measurements and will give the transition moment at a given internuclear distance directly,²²

$$R_{e}(\bar{r}_{v'v''}) = \left\{ \left(\frac{2 - \delta_{0,\Lambda''}}{2 - \delta_{0,\Lambda' + \Lambda''}} \right) \frac{f_{v'v''}}{1.5\kappa \ q_{v'v''} \ v_{v'v''}} \right\}^{1/2}, \tag{5}$$

where c is the speed of light and κ is as defined above in presenting Eq. (1). Each oscillator strength measurement results in a discrete point on a plot of transition moment as a function of internuclear separation.

The scaling factor, ζ , determined from Eq. (4) allows us to convert our relative transition-moment data into absolute units. Combining our absolute branching ratio data with the oscillator strength data allows us to extend the transitionmoment function, because all transitions involved in the oscillator strength measurements have *r* centroids smaller than 1.27 Å.

Plotting our renormalized data and the oscillatorstrength measurements together, showed that our data faired smoothly into the data of Bethke,⁹ who used low resolution absorption at high pressure, and of Farmer et al.8 who used the hook method. The higher resolution measurements of Hasson and Nicholls,9 however, give transition moments that appear to be about 25 to 30% too low. Our data, when normalized by Gadd and Slanger's lifetimes,⁶ could be reconciled with Hasson and Nicholl's results only if the transition-moment function were not monotonic, but rather turned over at about 1.3 Å and started to decrease at shorter internuclear separations. This functional behavior, however, would lead to radiative lifetimes for the higher vibrational levels that were much longer than those observed experimentally. Interestingly, if the lifetime of NO(B, v' = 0) were 3.1 µs, as was reported by Jeunehomme⁵ and by Brzozowski et al.,4 our function would favor Hasson and Nicholl's oscillator strengths over those of the other two groups. We believe Gadd and Slanger's lifetime determinations are more reliable than the other two, so we discounted Hasson and Nicholl's oscillator strengths when we made the functional fit to the extended data set.

A least-squares-fit to the combination of our adjusted $R_e(r)$ data between 1.27 and 1.60 Å with Bethke and Farmer *et al.*'s data from 1.22 to 1.26 Å gives R_e in Debye as

$$R_e(r) = 0.350 - 0.104\bar{r}_{v'v'} + 3.69 \times 10^4 \exp(-10.1 \ \bar{r}_{v'v'}).$$
(6)

Radiative lifetimes calculated from this function for v' = 0-5 are consistent with Gadd and Slanger's measurements to better than $\pm 4\%$. The radiative lifetime for v' = 6 that results from R_e described by Eq. (6) is about 17% too long. Table I lists the Einstein coefficients determined from this procedure along with other relevant information.

TABLE I. NO Beta-band Einstein coefficients.

<u> </u>							
v'	υ"	Wavelength	qv'v"	r centroid	Re(r)	Branching	
		nm	1	Δ	Debve	ratio	An'n"
		11111			Debye	Tatio	<i>N V</i>
0	0	220.09	0.000 02	1.269	0.3181	0.0001	5.269E + 01
	1	229.57	0.000 26	1.285	0.3014	0.0012	$6.029E \pm 02$
	2	220 72	0.001.76	1 302	0 2865	0.0046	2 200E + 02
	2	239.73	0.001 /0	1.302	0.2805	0.0000	3.290E + 0.5
	3	250.67	0.007 64	1.319	0.2735	0.0230	1.138E + 04
	4	262.46	0.023 54	1.336	0.2619	0.0565	2.802E + 04
	5	275.20	0.054.71	1 354	0.2517	0 1052	$5.216E \pm 04$
	2	275.20	0.004 71	1.554	0.2517	0.1052	5.210E + 04
	0	289.01	0.099 55	1.372	0.2425	0.1534	7.008E + 04
	7	304.01	0.145 34	1.391	0.2344	0.1798	8.914E + 04
	8	320.38	0.173 05	1.411	0.2271	0.1717	$8.513E \pm 04$
	å	229.79	0 160 96	1 433	0.2205	0.1350	6 602 E + 04
	9	330.20	0.109.80	1.432	0.2203	0.1350	0.092E + 04
	10	357.95	0.138 39	1.453	0.2145	0.0879	4.356E + 04
	11	379.64	0.093 92	1.475	0.2091	0.0475	2.353E + 04
	12	403.67	0.053.12	1 400	0.2040	0.0213	$1.054E \pm 0.0$
	12	403.07	0.05512	1. 777	0.2040	0.0215	1.0342 + 04
	13	430.42	0.024 99	1.524	0.1992	0.0079	3.901E + 03
	14	460.36	0.009 73	1.550	0.1947	0.0024	1.185E + 03
	15	494 08	0.003.11	1 579	0 1002	0.0006	$2027E \pm 02$
	15	+)+.00	0.005 11	1.579	0.1902	0.0000	2.527E + 02
	16	532.31	0.000 81	1.610	0.1858	0.0001	5.816E + 01
		Sum =	0.998 0				
	-						
I	0	,215.24	0.000 14	1.260	0.3283	0.0008	4.746E + 02
	1	224.30	0.001 69	1.276	0.3105	0.0079	4.530E + 03
	2	234.00	0 009 33	1 292	0 2949	0.0348	$1.986F \pm 04$
	2	237.00	0.007.55	1.272	0.2747	0.0070	
	3	244.40	0.031 21	1.309	0.2811	0.0929	5.297E + 04
	4	255.60	0.069 68	1.326	0.2688	0.1659	9.454E + 04
	5	267.67	0 107 25	1 343	0.2570	0.2048	1.167E + 05
	2	207.07	0.107 25	1.545	0.2379	0.2048	1.10/E + 0.5
	6	280.71	0.111 44	1.360	0.2484	0.1710	9.748E + 04
	7	294.85	0.069 50	1.378	0.2400	0.0859	4.899 <i>E</i> + 04
	8	310.21	0.015.32	1 304	0 2334	0.0154	8 770 F + 03
	0	224 27	0.015 52	1.574	0.2334	0.0134	8.7702 + 03
	9	326.97	0.002 78	1.432	0.2204	0.0021	1.211E + 03
	10	345.31	0.048 05	1.443	0.2173	0.0303	1.729E + 04
	11	365.45	0 112 08	1 463	0.2120	0.0568	$3.238F \pm 04$
	12	297 66	0.142 72	1 4 9 5	0.2060	0.0591	2 212 E + 04
	12	387.00	0.143 72	1.465	0.2069	0.0581	3.313E + 04
	13	412.27	0.127 20	1.508	0.2021	0.0408	2.326E + 04
	14	439.65	0.084 03	1.533	0.1975	0.0212	1.210E + 04
	15	470 31	0.042.80	1 560	0 1031	0.0084	A812E + 03
	15	470.31	0.042.00	1.500	0.1931	0.0084	4.012E + 03
	16	504.83	0.017 01	1.589	0.1888	0.0026	1.478E + 03
		Sum =	0.993 23				
•	•	A10 (7	0 000 50	1.0.50			a aa (च
2	0	210.67	0.000 59	1.232	0.3390	0.0035	2.286E + 0.3
	1	219.34	0.005 85	1.267	0.3202	0.0275	1.783E + 04
	2	228.60	0.025 54	1.283	0.3036	0.0952	$6.182E \pm 04$
	3	738 53	0.063.59	1 200	0.2800	0 1890	1227 E 05
	3	230.33	0.005 57	1.277	0.2390	0.1850	1.2272 + 05
	4	249.18	0.095 86	1.315	0.2760	0.2281	1.481E + 05
	5	260.63	0.082 26	1.332	0.2647	0.1573	1.021E + 05
	6	272.98	0.028 01	1.347	0.2553	0.0434	$2.815E \pm 04$
	7	286 33	0 000 28	1 369	0 2441	0.0003	$2.229E \pm 02$
	~	200.33	0.000 28	1.509	0.2441	0.0003	
	ð	500.80	0.03/36	1.389	0.2352	10201	2.382E + 04
	9	316.53	0.081 18	1.407	0.2286	0.0646	4.197E + 04
	10	333.69	0.062 42	1.425	0.2226	0.0402	2.610E + 04
	11	352 46	0.010.69	1 4 3 9	0 2182	0.0056	$3.643F \pm 03$
	10	272.40	0.000 (0	1 490	0.2102	0.0036	
	12	3/3.08	0.008 62	1.480	0.2079	0.0035	2.251E + 0.5
	13	395.81	0.069 86	1.496	0.2046	0.0228	1.479E + 04
	14	420.99	0.129 03	1.518	0.2002	0.0335	2.174E + 04
	16	440.02	0 122 74	1 542	0.1059	0.0074	1777 E + 04
	15	449.02	0.133 /4	1.343	0.1958	0.0274	1.77E + 04
	16	480.37	0.093 77	1.570	0.1915	0.0150	9.735E + 03
	17	515.66	0.052 70	1.594	0.1880	0.0066	4.260E + 03
		Sum -	0 981 34				
		Sum -	0.701 54				
3	0	206.35	0.001 75	1.244	0.3503	0.0105	7.665E + 03
	1	214.65	0.014.09	1.259	0.3302	0.0665	$4.873E \pm 04$
	÷.	222 50	0.017 (2	1.234	0.3302	0.1705	
	2	223.32	0.047.63	1.2/4	0.3127	0.1785	1.308E + 05
	3	233.00	0.084 14	1.290	0.2973	0.2517	1.845E + 05
	4	243.15	0.074 95	1.305	0.2838	0.1798	$1.318E \pm 05$
	, c	254.05	0.021.00	1 320	0 2720	0.0408	$2.991E \pm 0.4$
	2	2.54.05	0.021.00	1.520	0.2720	0.0400	2.7712 + 04
	6	205.77	0.002 69	1.350	0.2540	0.0040	2.895E + 03
	7	278.40	0.046 79	1.359	0.2491	0.0576	4.220E + 04
	8	292.07	0.063 90	1.375	0.2413	0.0639	$4.684E \pm 04$
	ň	206.97	0.019 57	1 200	0.2250	0.0152	
	7	300.87	0.018 37	1.330	0.2350	0.0152	1.113L + 04
	10	322.97	0.004 31	1.426	0.2221	0.0027	1.980E + 03
	11	340.52	0.054 40	1.436	0.2191	0.0283	2.074E + 04
	12	359 73	0.072.60	1 455	0 2141	0.0306	$2.247F \pm 04$
		557.15	J.J. 7 & UU	1.100	J.2171	0.0000	

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TABLE I. (continued).

			0.034.16	1 470	0 2000	0.0082	$6.044F \pm 03$
	13	380.82	0.024 16	1.4/2	0.2099	0.0082	0.0442 ± 0.000
	14	404.07	0.002 23	1.501	0.2035	0.0006	4.391E + 02
	15	429.82	0.058 66	1.530	0.1980	0.0124	9.085E + 03
	16	159 17	0 126 31	1 554	0 1941	0.0211	1.549E + 04
	10	430.47	0.120 31	1.554	0.1041	0.0177	$1.296E \pm 04$
	17	490.51	0.134 20	1.570	0.1900	0.0177	1.250E + 04
	18	526.54	0.097 10	1.604	0.1866	0.0099	7.263E + 03
		Sum =	0.949 48				
		Sum	0.7.77				
4	0	202.25	0.004 08	1.236	0.3619	0.0248	2.026E + 04
	1	210.23	0.026.50	1.250	0.3408	0.1271	1.039E + 05
	-	210.25	0.067.48	1 265	0 3224	0 2570	$2.102E \pm 05$
	2	218.72	0.007 48	1.205	0.5224	0.2376	1042 - 05
	3	227.79	0.078 12	1.280	0.3061	0.2375	1.943E + 03
	4	237.48	0.029 77	1.295	0.2926	0.0730	5.970E + 04
	5	247 87	0.000.70	1.308	0.2815	0.0014	1.143E + 03
	~	247.07	0.040.43	1 221	0.2649	0.0626	$5.123E \pm 04$
	0	259.01	0.040 43	1.331	0.2049	0.0020	5.1252 01
	7	271.00	0.053 44	1.346	0.2558	0.0674	5.512E + 04
	8	283.93	0.008 36	1.358	0.2494	0.0087	7.128E + 03
	õ	207 00	0.013.82	1 389	0 2355	0.0111	9.095E + 03
	9	297.90	0.015 82	1.502	0.2200	0.0291	3 116 F + 04
	10	313.05	0.057 57	1.403	0.2301	0.0381	5.110E + 04
	11	329.51	0.033 57	1.419	0.2246	0.0182	1.485E + 04
	12	347 46	0.000 15	1.438	0.2186	0.0001	5.361E + 01
	12	2(7.10	0.043.83	1 467	0.2110	0.0148	$1.209E \pm 04$
	13	367.10	0.042 82	1.407	0.2110	0.0140	1.207E + 0.4
	14	388.66	0.071 38	1.485	0.2069	0.0200	1.032E + 04
	15	412.42	0.023 97	1.502	0.2034	0.0054	4.433E + 03
	14	429 72	0.003.68	1 561	0 1929	0.0006	5.086E + 02
	10	438.75	0.005 08	1.501	0.1026	0.0076	6153E + 03
	17	467.98	0.054 20	1.563	0.1926	0.0075	0.133E + 03
	18	500.68	0.124 90	1.587	0.1890	0.0136	1.115E + 04
	19	537 43	0.132.20	1.615	0.1851	0.0112	9.151E + 03
	17	557.45 Sum	0.867.14				
		Sum =	0.867 14				
5	0	108 37	0 007 99	1 228	0.3742	0.0498	4.495E + 04
5		190.57	0.041.24	1.220	0.2520	0.2025	$1.837E \pm 05$
	1	206.03	0.041 34	1.242	0.3320	0.2035	1.6572 + 05
	2	214.19	0.076 33	1.257	0.3325	0.2984	2.693E + 05
	3	222.88	0.050 11	1.271	0.3157	0.1567	1.415 <i>E</i> + 05
	4	222:00	0.001.71	1 278	0 3089	0.0045	4.090E + 03
	4	232.13	0.001 71	1.276	0.5002	0.0045	4.522 E + 04
	5	242.06	0.025 53	1.306	0.2830	0.0501	4.525E + 04
	6	252.68	0.051 54	1.320	0.2726	0.0825	7.445E + 04
	7	264.07	0.010.50	1.332	0.2644	0.0139	1.251 <i>E</i> + 04
		204.07	0.012.00	1 240	0.2497	0.0123	$1.112F \pm 04$
	ð	270.33	0.012.09	1.500	0.2487	0.0125	2.924 E + 04
	9	289.55	0.050 49	1.373	0.2424	0.0425	3.834E + 04
	10	303.84	0.019 27	1.386	0.2365	0.0133	1.205E + 04
	11	310 33	0.005.38	1 421	0.2238	0.0029	2.596E + 03
	10	226.16	0.0051.02	1 4 2 1	0.2208	0.0228	$2.054F \pm 04$
	12	330.10	0.031 03	1.451	0.2208	0.0220	2.0342 + 04
	13	354.50	0.034 54	1.446	0.2163	0.0126	1.138E + 04
	14	374.57	0.000 23	1.472	0.2098	0.0001	6.043E + 01
	15	206 50	0.046.10	1 407	0 2043	0.0107	9.673E + 03
	15	390.39	0.040 10	1.777	0.2010	0.0106	1.125E + 0.4
	16	420.86	0.066 92	1.515	0.2008	0.0120	1.135E + 04
	17	447.70	0.022 37	1.531	0.1979	0.0034	3.062E + 03
	18	477 53	0.005 25	1.562	0.1927	0.0006	5.618E + 02
	10	£10.94	0.076.06	1 600	0 1871	0.0069	6.268E + 03
	19	510.04	0.070 00	1.000	0.1071	0.0007	
		Sum ==	0.654 /8				
6	^	104 69	0.012.69	1 220	0 3860	0.0869	$8.706E \pm 04$
0	0	174.00	0.013 08	1.220	0.3009	0.0000	2 700 E + 05
	1	202.06	0.055 52	1.235	0.3635	0.2780	2.790E + 05
	2	209.90	0.070 25	1.249	0.3431	0.2801	2.805E + 05
	3	218 23	0.018 75	1.262	0.3265	0.0602	6.032E + 04
	5	210.23	0.016 75	1 394	0 3034	0.0164	$1.640 F \pm 04$
	4	227.11	0.006 /0	1.204	0.3024	0.0104	
	5	236.59	0.047 15	1.296	0.2918	0.0950	9.511E + 04
	6	246.72	0.021 55	1.309	0.2811	0.0355	3.555E + 04
	7	257 58	0.004.06	1 3 3 6	0.2617	0.0051	5.105E + 03
	,	207.00	0.004 00	1 2/5	0.2017	0.0457	$4579F \pm 04$
	8	269.23	0.043 30	1.345	0.2505	0.0457	1.707 7 . 04
	9	281.76	0.019 79	1.358	0.2494	0.0172	1.72/E + 04
	10	295.28	0.005 12	1.390	0.2350	0.0034	3.446E + 03
	11	200.89	0.045 50	1 200	0 2315	0.0257	2.570E + 04
	11	307.00	0.045 50	1.377	0.2313	0.0001	0.107E + 02
	12	325.70	0.019 56	1.412	0.2267	0.0091	9.12/E + 03
	13	342.90	0.006 05	1.450	0.2154	0.0022	2.185E + 03
	14	361 64	0.051.24	1.459	0.2131	0.0154	1.543E + 04
	17	202.07	0.001 27	1 472	0.2005	0.0064	$6417F \pm 03$
	15	302.12	0.020 00	1.4/3	0.2095	0.0007	
	16	404.60	0.003 65	1.498	0.2041	0.0007	7.202E + 02
	17	429.33	0.048 24	1.527	0.1986	0.0075	7.541E + 03
	19	456 69	0.062.57	1.545	0.1955	0.0079	7.875E + 03
	10	407 07	0.002 07	1 550	0.1943	0.0008	$8 182F \pm 02$
	19	48/.0/	0.007.98	1.332	0.1943	0.0000	0.102E T 02
		Sum =	0.576 66				

TABLE II. Radiative lifetimes of NO($B^{2}\Pi, v'$).^a

v	Present results	Gadd and Slanger (Ref. 6)	Brzozowski et al. (Ref. 4)	Jeunehomme and Duncan (Ref. 5)	Robinson and Nicholls (Ref. 1) or Vilesov and Matveev (Ref. 2) ^b	Kuz'menko et al. (Ref. 3)	de Vivie and (Ref. 11)	Cooper (Ref. 10)	Langhoff et al. (Ref. 12)
0	2.02	2.00	3.1 + 0.2	3.1 ± 0.6	2.00	0.32	2.63	5.52	1.99
1	1.75	1.82	2.9 + 0.2	2.3 ± 0.3	2.02	0.35	2.32	4.49	1.79
2	1.54	1.52	2.8 + 0.2	2.2 ± 0.4	2.05	0.38	2.08	3.66	1.60
3	1.36	1.46	2.6 + 0.2	_	2.09	0.41	1.89	2.85	1.41
4	1.22	1.19	2.5 + 0.2		2.17	0.46	1.75	2.18	1.23
5	1.11	1.07	2.3 + 0.2		2.35	0.52	1.64	1.70	1.05
6	1.00	0.85	2.3 ± 0.2		2.41	0.55	1.53	1.34	0.87

*Units are 10⁻⁶ s.

 ${}^{b}R_{e}(r)$ normalized so that $\tau(v'=0) = 2.00 \times 10^{-6}$ s.

IV. DISCUSSION

A. Transition moment functions

Figure 4 compares our transition-moment function with others that have appeared in the literature. The three functions determined from *ab inito* calculations¹⁰⁻¹² behave qualitatively like our function, i.e., the value of the transition moment decreases with increasing internuclear separation. We had to divide Cooper's transition moment values by a factor of two in order to have a consistent degeneracy normalization between all sets of data.^{21,22}

Cooper's¹⁰ function decreases somewhat too steeply over the range common to both his function and ours, but appears to represent experimental oscillator strengths quite well. Over the range 1.3 to 1.45 Å, the relative variation of de Vivie and Peyerimhoff's¹¹ function is consistent with ours, to within a few percent. Their function, however, is inadequate at r < 1.3 Å and decreases too rapidly for r > 1.45 Å.

Langhoff *et al.* found, that if they shifted their *ab initio* function 0.025 Å to larger internuclear separations, they could reproduce Gadd and Slanger's radiative lifetimes for all vibrational levels up through v' = 6 to better than $\pm 4\%$. Langhoff *et al.* "shifted" transition-moment function agrees with ours to better than $\pm 4\%$ between 1.24 and 1.60 Å.

The three previously published, experimentally derived functions all predict a variation in transition moment with internuclear separation that is contrary to our findings. Kuz'menko *et al.*³ function results primarily from fits to absolute emission measurements in shock heated air.³³ Those experiments did not have sufficient sensitivity and spectral resolution to provide positive identification of the NO β bands. A chronic problem with shock-tube measurements is that they tend to be plagued by interference from impurity emissions. This effect results in absolute photon-emission rates that are too large.

The functions of Robinson and Nicholls¹ and Vilesov and Matveev² derive from an approach that is similar to ours, so rationalizing the differences between their findings and ours is not so straightforward. The three major sources of error in using a branching-ratio technique to construct a transition-moment function are (1) incorrect band intensity measurements, because of spectral overlap problems with impurity emissions or other vibrational levels of the band being studied; (2) incorrect values of Franck–Condon factors and r centroids; or (3) incorrect calibrations of the response of the detection system as a function of wavelength.

Our use of spectral fitting for determining band intensities reduces problems with spectral overlap significantly. These problems are most pronounced at longer wavelengths and could lead to overestimates of intensities of bands with larger r centroid values.

Robinson and Nicholls list the Franck-Condon factors



FIG. 4. Comparison between the various NO(B-X) transition-moment functions. Present results (—); Langhoff *et al.* (Ref. 12) (------); de Vivie and Peyerimhoff¹¹ (---); Cooper (Ref. 10) (----); Vilesov and Matveev (Ref. 2) (----); Bethke (Ref. 7) (O); Farmer *et al.* (Ref. 8) (Δ); Hasson and Nicholls (Ref. 9) (\Box).

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and r centroids used in their analysis. Although their values are based upon Morse potentials, they are similar to the values we used. Vilesov and Matveev's Franck–Condon factors and r centroids come from Jain and Sahni³¹ and also are almost identical to those used here.

Response calibration problems can result either from failure to fill monochromator optics or from neglect to correct standard lamp outputs from units of Watts to photons s^{-1} . Mixing intensity units tends to skew corrected intensities to be higher at longer wavelengths or larger *r* centroids. Underfilling monochromator optics can lead to response function errors if the photomultiplier varies in sensitivity across its face. Predicting how this effect will influence intensity measurements, however, is difficult.

Some sort of systematic error in the experiments of Robinson and Nicholls and Vilesov and Matveev seems likely. Dividing $R_e(\bar{r}_{v'v'})$ determined from their function by the wavelength of each transition gives relative branching ratios for v' = 0 to v'' = 2-16 that agree with ours to better than ± 5 percent.

B. Radiative lifetimes

Table II compares the radiative lifetimes derived from our transition-moment function with experimentally measured lifetimes and those determined from other proposed transition-moment functions. The agreement with the recent results of Gadd and Slanger⁶ is excellent for all vibrational levels except v' = 6. Most likely the cause of this discrepancy is because the function described by Eq. (6) does not increase rapidly enough below 1.25 Å.

Agreement with the radiative lifetimes determined by Brzozowski *et al.*⁴ and Jeunehomme and Duncan⁵ is, of course, not so good. Naturally, had we normalized our transition-moment function appropriately, some overlap between our calculated lifetimes and those measured by these two groups would have occurred. Our transition-moment function, however, indicates that the reduction in radiative lifetime with increasing vibrational level is much stronger than reported by Brzozowski *et al.*

Both Brzozowski *et al.* and Jeunehomme and Duncan monitored fluorescence decays following excitation in a pulsed discharge. A potential problem with this approach is the possibility that collisional or radiative cascade from higher states, that are also excited in the discharge, will continue to generate the state under study after termination of the discharge. This effect generally results in radiative lifetimes that are too long. Another potential problem is that radiation from the state under study might not be isolated adequately from radiation from other states. Neither of these potential problems will affect the measurements of Gadd and Slanger. They prepared the various vibrational levels of NO(B) by laser excitation. Thus, only one vibronic state was excited and only one radiated.

Table II also lists radiative lifetimes determined from other proposed transition-moment functions. The experimentally derived functions of Robinson and Nicholls,¹ Vilesov and Matveev,² and Kuz'menko *et al.*³ all predict that radiative lifetimes will increase with increasing vibrational level in contradiction to all radiative lifetime measurements. In addition, as noted above, the transition-moment function of Robinson and Nicholls or Vilesov and Matveev is inconsistent with absorption oscillator strength measurements.

Radiative lifetimes we compute from de Vivie and Peyerimhoff's and Cooper's ab initio functions are longer than those measured by Gadd and Slanger, although those we compute from de Vivie and Peyerimhoff's function are only 30 percent too long for v' = 0-3. We compute radiative lifetimes from de Vivie and Peyerimhoff's function that are shorter by a factor of $\sqrt{2}$ than the values they list in their Table VIII. Although the computations used to calculate Einstein coefficients are based upon the appropriate equation in their paper, we may have misinterpreted their normalization to account for degeneracy effects. For comparison with our function, the absolute value of their function is less important than the qualitative trends it predicts. In a relative sense, the lifetimes calculated from their function decrease with increasing vibrational level about 20 percent more slowly than ours. The major problem with their function. however, is that it doesn't predict the sharp increase in the transition-moment function that commences at about 1.25 Å.

In contrast to de Vivie and Peyerimhoff, Cooper's¹⁰ function predicts the sharp increase below 1.25 Å, but his function doesn't flatten out enough at larger internuclear separations. As a result, his function predicts a much greater change in radiative lifetime with vibrational level than is observed experimentally.

As noted above, Langhoff *et al.*'s calculations predict both the magnitude and the variation in radiative lifetime with increasing vibrational level to within about $\pm 4\%$ for all vibrational levels, v' = 0-6.

C. Other issues

Gadd and Slanger excited NO(B,v' = 6) with a laser and scanned the resulting fluorescence spectrum. They converted the relative intensities to a set of branching ratios from v' = 6 to ground-state vibrational levels. These branching ratios then were converted to absolute Einstein coefficients by dividing each by the measured radiative lifetime of v' = 6.

Our Einstein coefficients for v' = 6 to v'' = 0 to 3 and 5 are within $\pm 10\%$ of Gadd and Slanger's. For all other transitions, Gadd and Slanger's values are larger than ours by factors ranging from 1.3 to 4. We see some evidence that a systematic error in Gadd and Slanger's measurements is the cause of the discrepancies.

Figure 5 shows the ratio of Gadd and Slanger's Einstein coefficients to ours plotted as a function of the wavelength of each transition. The ratios for the first fourteen transitions separate themselves into three distinct groups. The transition having Einstein coefficients on the order of 10^5 s^{-1} are the ones that agree with ours to within $\pm 10\%$. Those transitions for which A_{6,v^*} is on the order of 10^4 s^{-1} have ratios near 1.5, while the ratios are roughly 2.5 for transition having $A_{6,v^*} \sim 10^3 \text{ s}^{-1}$. This grouping of discrepancies according to the magnitude of the Einstein coefficient suggests an incomplete baseline subtraction for the weaker bands, or per-



FIG. 5. Variation in the ratio of Einstein coefficients from v' = 6 to v'' = 0through 16 calculated by Gadd and Slanger to those we have derived, as a function of transition wavelength. O, $A_{6,e^*} \sim 10^5$ s⁻¹; Δ , $A_{6,e^*} \sim 10^4$ s⁻¹; \Box , $A_{\rm b} \sim -10^{\circ} {\rm s}^{-1}$.

haps, a nonlinearity in changing signal amplifier ranges.

Figure 5 also shows evidence of a second systematic error in Gadd and Slanger's measurements. The ratios for the two groups of transitions having Einstein coefficients on the order of 10^4 and 10^3 s⁻¹ increase linearly with increasing wavelength and, in addition, have similar slopes. The ratios of the 10⁵ s⁻¹ group decrease slightly with increasing wavelength. These trends could result from an error in calibrating the relative response of their monochromator as a function of wavelength. This seems likely since dividing the ratios of Gadd and Slanger's $A_{6\nu}$ to those we have derived by the transition wavelength results in a set of values that are constant to within $\pm 5\%$ both for the $10^4 \, \text{s}^{-1}$ group and for the 10^3 s⁻¹ group. Interestingly, the discrepancies in the Einstein coefficient ratios scale with wavelength in the same manner as the discrepancies between our transition-moment function and those of Robinson and Nicholls and Vilesov and Matveev.

Gadd and Slanger computed a set of radiative lifetimes for v' = 0 through 5 using the branching ratios for the v', 0transitions calculated by Langhoff et al. and the oscillator strengths measured by Hasson and Nicholls9 and by Farmer et al.8 They found generally good agreement with their measured radiative lifetimes, especially with those lifetimes calculated from Hasson and Nicholls' oscillator strengths. As we have already noted, our transition-moment function is incompatible with transition moments derived from Hasson and Nicholls oscillator strength measurements. Einstein coefficients calculated from these measurements, therefore, ought also to be incompatible with our measurements. Our

radiative lifetimes, however, agree rather well with those of Gadd and Slanger.

We don't understand how Gadd and Slanger arrived at the lifetime values they calculated. We wonder if a systematic error might explain the discrepancy between the radiative lifetimes we calculate from both sets of oscillator-strength measurements and those calculated by Gadd and Slanger. We find that the ratio of the lifetimes we calculate to those calculated by Gadd and Slanger is 1.62 to within 2.5% for all transitions. The constancy in the ratio shows that our branching ratios for the A_{v0} are compatible with those used by Gadd and Slanger. Since Hasson and Nichols and Farmer et al. list both oscillator strengths and Einstein coefficients for each transition, computational errors in converting from one quantity to the other also should not be an issue. The discrepancy of 1.62 (which just happens to be $16/\pi^2$) remains to be discovered.

V. SUMMARY

We have used a branching ratio technique to establish the variation in the electronic transition moment as a function of internuclear separation for the NO($B^2\Pi - X^2\Pi$) system. Although our transition-moment function differs significantly from previously published empirical functions, our function agrees to better than \pm 5% with the best available measurements of radiative lifetimes,6 of absorption oscillator strengths,^{7,8} and with the most recent and detailed ab initio computation.¹²

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