Einstein coefficients and transition moment variation for the NO(A $^2\Sigma^+$–X $^2\Pi$) transition

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Branching ratio measurements for the NO γ bands excited by energy transfer from metastable nitrogen molecules show that the electronic transition moment for the NO(A $^2\Sigma^+$–X $^2\Pi$) transition varies by about 40% over the r-centroid range of 1.13–0.97 Å. Combining this transition-moment variation with radiative lifetime measurements provides a complete set of Einstein coefficients for NO(A–X) transitions from $v' = 0$–2.

I. INTRODUCTION

The issue of whether or not the NO(A $^2\Sigma^+$–X $^2\Pi$) electronic transition moment varies significantly with r centroid has been the subject of a number of papers over the last several decades.[1-12] While a number of papers have shown evidence of a significant transition-moment variation,[1-6] several groups have disputed this contention.[7-12] References 6 and 10 review most of the relevant literature. The general consensus in the scientific community seems to be that no significant transition-moment variation occurs for the NO γ bands. Recently, while studying the eletronic energy transfer between N$_2$(A $^3\Sigma_u^+$) and NO,[13,14] we found inconsistencies in NO(A $^2\Sigma^+$) excitation rates measured using different bands originating from $v' = 0$ if we invoked a constant transition moment. The excitation of the NO γ bands by N$_2$(A $^3\Sigma_u^+$) energy transfer to NO(X $^2\Pi$) provides a source of γ-band emission which is free from other significant overlapping band systems in the spectral region. We find that our observed branching ratios for transitions from a common vibrational level in the upper state cannot be explained by variations in the Franck–Condon factors. Our observations show variations in the electronic transition moment of more than 40% over the r-centroid range 1.13–0.97 Å.

Correct transition probabilities for the NO(A–X) system bear directly upon atmospheric science through such processes as the measurement of NO column densities in the mesosphere[15] or the interpretation of emissions in a strong aurora. In addition proper NO(A–X) transition probabilities are needed to calculate the gain for various transitions in the optically pumped NO(A–X) laser.[16] Correct NO(A–X) transition probabilities affect a wider range of studies, however. Because they are easy to excite, the NO γ bands are often used to establish the relative spectral response of monochromators in the ultraviolet.[7,9] Using incorrect branching ratios for the A–X transition will of course result in an incorrect response function, and will thereby invalidate all other measurements which depend upon the spectral response determined from the γ-band branching ratio measurements. The technique of laser-induced fluorescence on NO(A–X) transitions has become an increasingly important tool for probing the vibrational distributions of ground electronic state NO produced in chemical or photolytic reactions.[17,18] Incorrect values for the NO(A–X) transition probabilities invalidates the results of these measurements, and thereby casts doubt on the validity of dynamical interpretations of the results.

II. EXPERIMENTAL

The apparatus used in these studies has been described in detail in a number of other papers.[13,14,19-23] Briefly, the experiment involved exciting the NO γ bands in the energy-transfer reaction between N$_2$(A $^3\Sigma_u^+$) and NO in a discharge–flow apparatus. Adding nitrogen molecules to a flow of metastable argon atoms produced N$_2$(A) molecules in the absence of significant number densities of nitrogen atoms or N$_2$(X,v).[24-26] A low-power, dc discharge through a flow of argon atoms generated the argon metastables. NO was added to the flow downstream from the nitrogen addition inlet and the resulting spectrum was recorded photoelectrically at moderate resolution ($\Delta\lambda = 0.33$ nm) between 200 and 400 nm. A least-squares spectral fitting procedure determined the intensities of each band.[22] Standard quartz–halogen and D$_2$ lamps were used to determine the relative response of the spectral system as a function of wavelength. Excellent agreement between observed and calculated intensities of a number of bands of the N$_2$(A $^3\Sigma_u^-$–X $^1\Sigma_g^+$) and N$_2$(C $^3\Pi_u$–B $^3\Pi_g$) systems between 220 and 400 nm confirmed the reliability of the calibration.

III. RESULTS AND DISCUSSION

The intensity of emission from a given band is the product of the number density in the upper state and the Einstein coefficient for spontaneous radiation. The Einstein coefficient can be separated into a product of the Franck–Condon factor, the cube of the transition frequency, and the square of the electronic transition moment. Thus

$$I_{v'v''} = N_{v'}A_{v'v''} \propto N_{v'}q_{v'v''}\nu_{v'v''}^3 |R_e(\bar{r}_{v'v''})|^2. \tag{1}$$

The constant-moment population in the upper state is then determined from the ratio of the integrated band intensity to the product of the Franck–Condon factor and the cube of the transition frequency

$$N_{v'v''}^* = \frac{I_{v'v''}}{q_{v'v''}\nu_{v'v''}^3} = N_{v'}|R_e(\bar{r}_{v'v''})|^2. \tag{2}$$

The ratios of these constant-moment populations to each other should be unity unless the transition moment varies

with r centroid. The relative variation in the transition moment with r centroid results from the ratio of the various constant-moment populations to one reference population. Scaling the relative transition moments to experimentally determined lifetime or oscillator-strength data is then a relatively simple process.

We determined the constant-moment populations of the bands emanating from $v' = 0$ and 1 using a spectral fitting routine for each Δv sequence from $\Delta v = 1$ to $\Delta v = -8$. The fitting routine corrected for spectral overlap between the transitions for $v' = 0$ and 1. The fit included the different effective rotational temperatures for the two vibrational levels.[14] We ratioed each of these populations to the ones determined for the $\Delta v = -3$ sequence. This sequence is in the middle of the wavelength range for the band system and thus should minimize any systematic errors in the relative monochromator response function. The Franck–Condon factors of both Nicholls[27] and Albritton et al.[28] gave similar results. Our final results incorporate the latter set.

Figure 1 shows the electronic transition moment relative to its value for the $\Delta v = -3$ sequence plotted against r centroid. The variation is small, but consistent, up through the $\Delta v = -3$ sequence, but rises much more sharply for the $\Delta v < -3$ sequences. The diamonds in Fig. 1 show our reanalysis of the branching-ratio measurements of McGee et al.[11] They excited NO($A,v' = 0$) with a laser and reported relative band emission intensities. Their results agree excellently with ours. Finally, we have also plotted the transition moment variation given by Brzozowski et al.[5] who observed γ-

band emission in electron–beam excited NO during studies on NO predissociation.

We fit the results of the three experiments to a quadratic function of r centroid:

$$|R_e\,(\bar{r}_{v'v''}\,)|_{\rm rel} = 33.08 - 58.77\,\bar{r}_{v'v''} + 26.85\bar{r}^2_{v'v''}. \qquad (3)$$

Using this functional form for the relative transition moment, we determined a smoothed set of branching ratios for emission from a given upper state as being

$$B_{v'v''} = \frac{q_{v'v''}\,\nu^3_{v'v''}\,|R_e\,(\bar{r}_{v'v''}\,)|^2_{\rm rel}}{\sum\limits_{v''} q_{v'v''}\,\nu^3_{v'v''}\,|R_e\,(\bar{r}_{v'v''}\,)|^2_{\rm rel}}. \qquad (4)$$

The Einstein coefficient for spontaneous radiation from each band is the product of the branching ratio for the given band and the reciprocal of the radiative lifetime of the upper state vibrational level. The average of nine apparently reliable determinations of the fluorescence lifetime of NO($A,v' = 0$) gives a value of (202 ± 14) ns.[8,10,29–35] Eight different determinations for the $v' = 1$ level give a value of (192 ± 14) ns.[10,29,30,33,34,36–38] In both cases the error bars represent one standard deviation. Table I lists the Einstein coefficients for each band.

Equation (5) relates the Einstein coefficient for a given $v'v''$ transition to the absorption oscillator strength:

$$f^{\rm abs}_{v'v''} = \frac{m_e c\lambda^2_0}{8\pi^2 e^2}\frac{d_u}{d_1}A_{v'v''}. \qquad (5)$$

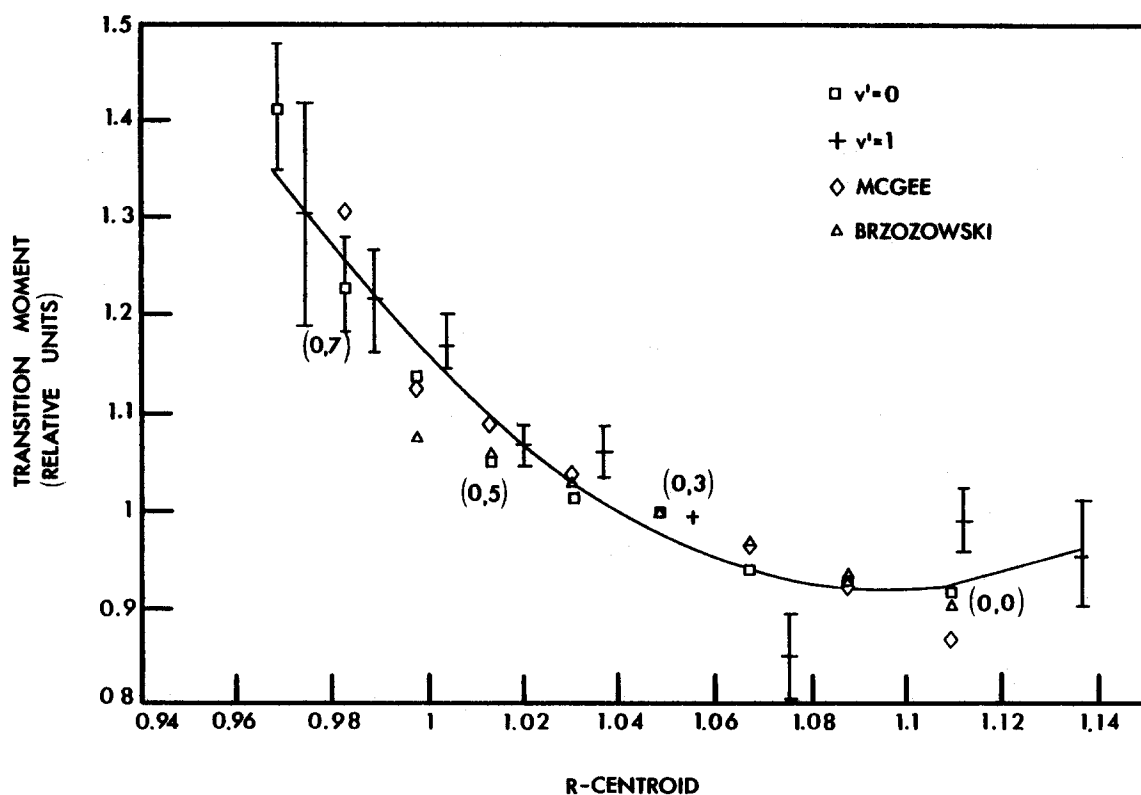Here m_e is the electron mass, e its charge in esu, c the speed

FIG. 1. Variation in electronic transition moment with r centroid for the NO(A $^2\Sigma^+$–X $^2\Pi$) transition.

TABLE I. Einstein coefficients for NO(A $^2\Sigma^+$–X $^2\Pi$).

v''	Wavelength (nm)	$Q_{v'v''}$	$\bar{r}_{(v'v'')}$ (Å)	$R_e(r)$	Branching ratio	$A_{v'v''}$ (s^{-1})
$v' = 0$						
0	226.548	0.166 97	1.1091	0.921 429	0.202 462	1.002E + 06
1	236.604	0.263 45	1.0873	0.917 005	0.277 740	1.375E + 06
2	247.421	0.236 46	1.067	0.935 830	0.227 041	1.124E + 06
3	259.087	0.159 62	1.0481	0.973 248	0.144 364	7.147E + 05
4	271.700	0.090 505	1.0303	1.026 027	0.078 883	3.905E + 05
5	385.377	0.045 696	1.0135	1.091 448	0.038 894	1.925E + 05
6	300.252	0.021 285	0.9977	1.166 803	0.017 777	8.801E + 04
7	316.482	0.009 363	0.9827	1.250 746	0.007 673	3.799E + 04
8	334.256	0.003 954	0.9684	1.342 021	0.003 166	1.568E + 04
9	353.794	0.001 622	0.9548	1.439 015	0.001 259	6.235E + 03
10	375.362	0.000 652	0.9419	1.540 195	0.000 485	2.405E + 03
11	399.283	0.000 259	0.9295	1.645 876	0.000 183	9.061E + 02
12	425.947	0.000 102	0.9177	1.754 110	0.000 067	3.339E + 02
$v' = 1$						
0	215.134	0.333 53	1.1364	0.962 957	0.451 795	2.353E + 06
1	224.182	0.102 95	1.1108	0.922 847	0.113 188	5.895E + 05
2	233.870	0.000 97	1.0920	0.915 801	0.000 925	4.818E + 03
3	244.266	0.072 31	1.0754	0.925 357	0.061 794	3.218E + 05
4	255.446	0.133 81	1.0551	0.957 153	0.106 972	5.572E + 05
5	267.499	0.132 57	1.0368	1.004 782	0.101 704	5.297E + 05
6	280.526	0.097 792	1.0198	1.065 139	0.073 099	3.807E + 05
7	294.644	0.060 554	1.0039	1.135 635	0.044 406	2.313E + 05
8	309.990	0.033 426	0.9888	1.215 151	0.024 100	1.255E + 05
9	326.723	0.017 042	0.9745	1.301 742	0.012 043	6.273E + 04
10	345.032	0.008 212	0.9609	1.394 282	0.005 653	2.944E + 04
11	365.139	0.003 800	0.9480	1.491 236	0.002 524	1.315E + 04
12	387.312	0.001 71	0.9357	1.592 003	0.001 084	5.651E + 03
13	411.871	0.000 753	0.9238	1.697 225	0.000 451	2.352E + 03
14	439.206	0.000 327	0.9126	1.803 203	0.000 182	9.507E + 02
15	469.796	0.000 141	0.9017	1.912 810	0.000 072	3.769E + 02
$v' = 2$						
0	204.952	0.292 46	1.1654	1.050 907	0.468 229	2.573E + 06
1	213.147	0.017 314	1.1516	1.003 423	0.022 467	1.234E + 05
2	221.886	0.156 06	1.1194	0.932 396	0.154 996	8.516E + 05
3	231.223	0.072 89	1.0947	0.915 646	0.061 695	3.390E + 05
4	241.217	0.000 38	1.0770	0.923 791	0.000 288	1.584E + 03
5	251.936	0.034 722	1.0644	0.939 840	0.023 936	1.315E + 05
6	263.459	0.087 71	1.0440	0.983 897	0.057 946	3.184E + 05
7	275.873	0.104 21	1.0265	1.039 499	0.066 934	3.678E + 05
8	289.281	0.088 733	1.0103	1.105 627	0.055 919	3.072E + 05
9	303.801	0.062 245	0.9951	1.180 487	0.038 608	2.121E + 05
10	319.569	0.038 476	0.9807	1.262 851	0.023 464	1.289E + 05
11	336.744	0.021 789	0.9671	1.350 863	0.012 995	7.140E + 04
12	355.514	0.011 589	0.9542	1.443 523	0.006 707	3.685E + 04
13	376.099	0.005 891	0.9419	1.540 195	0.003 278	1.801E + 04
14	398.761	0.002 897	0.9301	1.640 572	0.001 534	8.432E + 03
15	423.818	0.001 392	0.9189	1.742 761	0.000 693	3.808E + 03
16	451.643	0.000 688	0.9081	1.847 680	0.000 304	1.672E + 03

of light, λ_0 the transition wavelength, and d_u and d_l are the electronic degeneracies of the upper and lower states, respectively. These last quantities are 1 and 2 for A $^2\Sigma^+$ and X $^2\Pi$, respectively. Applying our Einstein coefficients to Eq. (5) gives absorption oscillator strengths for the 0,0 and 1,0 bands of $(3.9 \pm 0.3) \times 10^{-4}$ and $(8.2 \pm 0.6) \times 10^{-4}$, respectively. These values agree excellently with literature measurements of $(4.03 \pm 0.22) \times 10^{-4}$ for the 0,0 transition (five different experiments)[39–43] and $(8.26 \pm 0.48) \times 10^{-4}$ for the 1,0 transition (three different measurements).[40,42,43] Thus our transition moment function satisfies the important

criterion that the lifetime and absorption measurements be consistent.

We have also calculated Einstein coefficients for $v' = 2$ assuming the transition moment variation of Eq. (3) and a radiative-decay lifetime for $v' = 2$ of (182 ± 10) ns.[10,29,30,33,34] Because the transition moment variation was extrapolated to regions outside the fit, the transition probabilities from $v' = 2$ are less reliable. This may be reflected in the modest disagreement between the absorption oscillator strength of the 2,0 band calculated from the transition probabilities given in Table I of $(8.1 \pm 0.4) \times 10^{-4}$ and the ex-

perimental value of $(6.8 \pm 0.2) \times 10^{-4}$.[40,42,43] Better agreement with the 2,0 band absorption measurements results from having the transition moment become constant at r-centroid values greater than 1.1 Å but with the same transition moment variation shown in Fig. 1 for smaller r-centroid values. This adjustment degrades the agreement with the 0,0 and 1,0 oscillator strengths slightly, however. We do not feel the accuracy of the oscillator strength measurements, probably about 20% for any individual measurement, justifies making such an adjustment for an apparent 16% discrepancy.

An apparent transition-moment variation could also be the result of our having an incorrect relative monochromator response function. In that case our analysis for the transition moment function would also be invalid. This does not appear to be a significant problem in our work, however, because we very accurately fit the Vegard–Kaplan (A $^3\Sigma_u^-$–X $^1\Sigma_g^+$) and second-positive (C $^3\Pi_u$–B $^3\Pi_g$) bands of nitrogen over the same wavelength region. In addition, the good agreement between our own results and those of the two other groups alluded to previously[5,11] confirms that our wavelength response function is accurate. Recently McGee et al.[44] published branching ratios for NO($A,v' = 1$) transitions. These measurements also agree quite well with the results presented here when properly analyzed to show the transition-moment variation.

ACKNOWLEDGMENTS

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