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**ELECTRON-IMPACT EXCITATION  
OF NITRIC OXIDE**

**BY**

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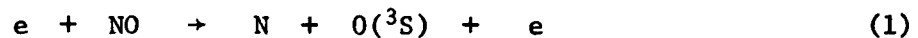
## Abstract

The absolute cross sections for the excitation of the  $\text{NO}^+$  Baer-Miescher bands ( $A^1\Pi_u \rightarrow X^1\Sigma_g^+$ ), two nitric oxide  $\beta'$  bands ( $B'^2\Delta_1 \rightarrow X^2\Pi_r$ ), and several atomic nitrogen multiplets in the vacuum ultraviolet by electron impact on NO have been measured over an energy range extending from threshold to 300 eV. The variation of the dipole transition moment for the  $\text{NO}^+$  ( $A^1\Pi_u \rightarrow X^1\Sigma_g^+$ ) band system was also determined.

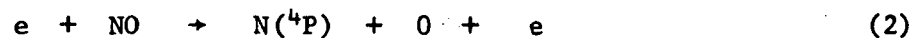
## INTRODUCTION

In a recent rocket experiment Zipf et al.<sup>1</sup> observed large concentrations of nitric oxide in an intense auroral arc. From 100 - 130 km the nitric oxide and molecular oxygen densities were found to be comparable in magnitude, and the ion composition within the auroral form was profoundly altered as a result of a large NO abundance. This experiment confirmed the implications of earlier ion mass spectrometer measurements<sup>2</sup> which had indicated the presence of enhanced NO concentrations in post-breakup aurora. It now appears that nitric oxide is a major neutral constituent in many auroral forms so that the excitation of NO by secondary electrons may be expected to contribute significantly to the emission spectrum of an aurora.

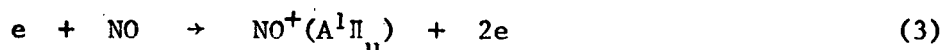
In particular the possibility now arises that the atomic oxygen and nitrogen lines observed as vacuum ultraviolet emission features in auroras<sup>3,4,5</sup> are due in part to dissociative excitation of NO by electron impact. For example, the dissociative excitation of the OI and NI resonance states



and



may be particularly important. It also seems likely that the  $\text{NO}^+$  Baer-Miescher bands ( $A^1\Pi_u \rightarrow X^1\Sigma_g^+$ ) would be excited by electron impact in a manner analogous to the  $\text{N}_2^+$  first negative bands<sup>6</sup> which appear prominently in the visible spectrum of an aurora.<sup>7</sup> This process, which involves simultaneous ionization and excitation of nitric oxide,



might contribute significantly to the auroral spectrum in the vacuum ultraviolet wavelength region 1250 - 1800Å.

In this paper we describe a laboratory study of the vacuum ultraviolet emission features which can be excited by electron impact on  $\text{NO}$ . As part of this investigation we measured the absolute excitation cross sections for the principal molecular and atomic emission features in the wavelength region 1100 - 1700Å that are produced in this manner, and we determined the variation of the dipole transition moment for the  $\text{NO}^+(A^1\Pi_u \rightarrow X^1\Sigma_g^+)$  band system. These results now permit a critical assessment of the role of nitric oxide as a source of ultraviolet photons in an auroral display.

Our results apply only to the excitation of states which are de-excited in processes which result in VUV radiation within a fairly short time (~ 8 microseconds). Holland and Maier<sup>8</sup> have recently reported the observation of long-lived states of  $\text{NO}^+$  which result in emission whose appearance is very similar to that of the  $\text{NO}^+$  (A-X) bands. These long-lived

states will also make a contribution to the VUV spectra of the upper atmosphere.

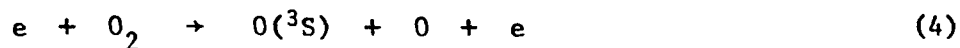
#### EXPERIMENTAL TECHNIQUES

The apparatus used in making these measurements has been described in detail by Mumma and Zipf<sup>9</sup> (see Figure 1). A small collision chamber, which was located in a large, rapidly pumped vacuum chamber, was filled with nitric oxide to a pressure of approximately  $1 \times 10^{-4}$  torr. An electron gun provided a monochromatic beam of electrons whose energy could be varied from 5 to 340 eV. The electron beam passed through the gas in the collision chamber and was collected by a positively-biased electron trap on the opposite side. The current to the electron trap, as well as stray currents to the top, bottom, and side wall of the collision chamber, were monitored. Checks were made to ensure that effects due to secondary and reflected electrons were negligible. Photons emitted in the interaction region were observed at  $90^\circ$  to the direction of the electron beam with a one-meter, normal incidence vacuum monochromator and a EMR 541GX solar-blind photomultiplier tube. All apertures in the detection system, except that on the photomultiplier tube, were windowless. Pulse counting and signal averaging techniques were used to improve the quality of the primary cross section data. The nitric oxide gas (CP grade) was obtained from Air Products and Chemicals, Inc. This gas was passed through a dry-ice cold trap to reduce the concentrations of other nitrogen oxides; this procedure left  $N_2$  as the principal contaminant ( $\sim 1\frac{1}{2}\%$ ).

The relative spectral response of the optical system was determined by using the method of molecular branching ratios. In the wavelength region 1300 - 1700Å the spectral response was inferred from the measured emission rates of the LBH bands of molecular nitrogen [ $N_2(a^1\Pi_u \rightarrow X^1\Sigma_g)$ ] using a method identical to that of Mumma and Zipf<sup>10</sup>. The spectral response of our monochromator and detector in the region 1100 - 1600Å was determined by exciting hydrogen deuteride with argon resonance radiation thereby producing Lyman-band fluorescence [ $HD(B^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+)$ ]. This absolute calibration technique has been described in detail by Becker et al.<sup>11</sup> The HD calibration was performed by placing an argon light source one inch from the optic axis, as shown in Figure 1, so that the fluorescing gas was visible to the monochromator through the back window of the collision chamber. Thus the detection geometry was nearly identical for the fluorescence and electron impact experiments. Figure 2 shows the relative spectral response of our optical system obtained using these techniques.

Absolute values for the excitation cross sections were deduced from the measured emission rates by comparison with the intensity of the atomic oxygen emission feature at 1304Å [ $OI(^3S \rightarrow ^3P)$ ]. Lawrence<sup>12</sup> has studied the excitation of this multiplet by electron impact on NO and assigned a cross section value of  $1.14 \times 10^{-18} \text{cm}^2$  at 100 eV for this excitation process (1). We have adopted Lawrence's result as a standard. It should be noted, however, that in the same research Lawrence found a cross section value for the process





which is 20% lower than the result obtained for the same quantity by Mumma and Zipf.<sup>9</sup> If we were to assume that Lawrence's measured cross section for process (1) is 20% low, and scale our NO cross section results accordingly, then the NO<sup>+</sup> Baer-Miescher band cross sections determined in this study would be in nearly exact agreement with the recent results obtained by Aarts and de Heer.<sup>13</sup>

## RESULTS

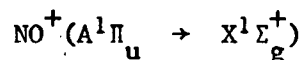
The vacuum ultraviolet spectrum of NO, excited by the impact of 100 eV electrons, consists almost entirely of the Baer-Miescher bands of NO<sup>+</sup> and the atomic multiplets of oxygen and nitrogen produced by dissociative excitation. At lower electron energies, the spectrum also contains bands of NO β' band system. Figure 3 shows the observed electron-impact spectrum of nitric oxide at 100 eV impact energy and 3.3 Å resolution. Two NO β' bands (dotted) are shown as they appeared at 30 eV impact energy. The dashed curve indicates the relative spectral response of the optical detection system.

The excitation function<sup>14</sup> for the (0,2) band of the [NO<sup>+</sup>(A<sup>1</sup>Π<sub>u</sub> → X<sup>1</sup>Σ<sub>g</sub><sup>+</sup>)] system is shown in Figure 4 from threshold to 300 eV. Similar results were obtained for bands from other vibrational levels of the upper electronic state. The excitation function obtained for the (4,0) band of the NO β' system is also shown in Figure 4. The excitation function for the atomic nitrogen resonance multiplet

[NI( $^4P \rightarrow ^4S$ )] excited dissociatively is shown in Figure 5.

In Table I we summarize the results of our absolute cross section measurements for electron impact on NO at 100 eV. The excitation cross sections for the multiplets of atomic nitrogen have been corrected for the effects of a small amount of molecular nitrogen ( $\sim 1\frac{1}{2}\%$ ) contained in the nitric oxide sample. Our results for the NO $^+$  Baer-Miescher bands are in good agreement with the recent measurements of Aarts and de Heer.<sup>13</sup> Our cross section values for the atomic nitrogen emission features at 1243 $\text{\AA}$  and 1493 $\text{\AA}$  agree within the experimental error with the results of Mentall<sup>15</sup> when allowance is made for typographical errors in Table I and Figure 1 of his paper. For the NI resonance multiplet, however, we obtain a dissociative excitation cross section nearly one half the value reported by Mentall.

#### 1. Variation of the Dipole Moment for the Transition:



The probability of a radiative transition from the  $v'$ th vibrational level of an upper electronic state to the  $v''$ th vibrational level of the lower electronic state can be written in the form

$$A_{v',v''} = C q_{v',v''} v^3 R_e^2(\bar{r}_{v',v''}) \quad (5)$$

where  $C$  is a constant,  $q_{v',v''}$  is the Franck-Condon factor for the two vibrational levels concerned,  $v$  is the wave number of the radiation

emitted, and  $R_e$  is the dipole transition moment.

The variation of the dipole transition moment, which is a function of the internuclear distance [here represented by the r-centroid,  $\bar{r}_{v',v''}$ ], can be studied experimentally by making accurate measurements of the absolute band intensities  $I_{v',v''}$ . For an optical system such as that shown in Figure 1,

$$I_{v',v''} = C' N_{v'} A_{v',v''} R_\lambda \quad (6)$$

where  $N_{v'}$  is the density of molecules in the  $v'$ th vibrational level of the upper state,  $A_{v',v''}$  is the absolute transition probability,  $R_\lambda$  is the relative response of the detection optics as a function of wavelength, and  $C'$  is a constant that depends on the excitation and detection geometry.

By measuring the intensity of the bands originating from a common vibrational level of the upper state ( $v'$  fixed), the relative dipole transition moment can be inferred as a function of  $\bar{r}_{v',v''}$  from the proportion

$$R_e(\bar{r}_{v',v''}) \propto (I_{v',v''}/R_\lambda q_{v',v''} v^3)^{1/2} \quad (7)$$

Tables of Franck-Condon factors and r-centroids for the Baer-Miescher bands [ $\text{NO}^+(\text{A}^1\Pi_u - \text{X}^1\Sigma_g^+)$ ] have been computed by Albritten et al.<sup>16</sup> based on RKR potential curves. These numbers differ somewhat from the Franck-Condon factors computed earlier by Nicholls<sup>17</sup>

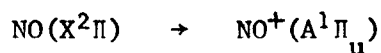
and by Wentink and Spindler<sup>18</sup> which are based on Morse potentials. The data of Albritten et al.<sup>16</sup> have been used to compute relative values for the dipole transition moment for the  $\text{NO}^+(\text{A} \rightarrow \text{X})$  bands from our intensity measurements. These transition moments are plotted in Figure 6 as a function of the corresponding  $r$ -centroids for the  $(0, v')$  and  $(1, v')$  progressions. The independent sets of data have been normalized to one another by a computer routine, which also generated the solid line as a least-squares fit to the data points. The curve is the graph of the relation

$$\log_{10} R_e = 9.265 (1 - 1.619 \bar{r}_{v', v''} + 0.6308 \bar{r}_{v', v''}^2) \quad (8)$$

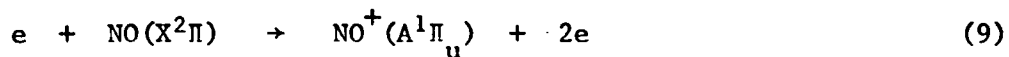
where  $\bar{r}_{v', v''}$  is given in Angstroms.

Using the variation of the dipole transition moment thus measured, we determined the relative transition probability for each band with a common upper state ( $v'$  constant) from Equation (5). Table II presents the results of this calculation. For convenience the results are normalized so that the sum of each row is unity.

## 2. Variation of the Dipole Moment for the Transition:



In the Born approximation the cross section for excitation of the  $v'$ th vibrational level of the upper state of an ion due to simultaneous ionization and excitation of neutral molecules in the ground state, viz.



can be expressed as follows

$$\sigma_{v'} = C'' q_{v',0} R_e^2(\bar{r}_{v'},0) \quad (10)$$

where  $C''$  is a constant,  $q_{v',0}$  is the Franck-Condon factor for the ionizing transition,  $\bar{r}_{v',0}$  the corresponding  $r$ -centroid value and  $R_e$  is the dipole transition moment. Using the cross sections listed in Table I and the relative transition probabilities given in Table II we determined  $\sigma_{v'}$  for four vibrational levels of the  $\text{NO}(A^1\Pi_u)$  when NO is excited by 100 eV electrons. The results of this calculation can be found in Table III.

If the  $\text{NO}^+(A^1\Pi_u)$  state is populated only by direct excitation, the variation of the dipole transition moment for process (9) can be determined from our values for  $\sigma_{v'}$  in a manner similar to that adopted in our analysis of the radiative transition  $\text{NO}^+(A \rightarrow X)$ . Hesser's<sup>19</sup> lifetime data implies that cascading is not important at least for the  $v' = 0$  level, and we have proceeded on this assumption. Franck-Condon factors and  $r$ -centroid values for the ionizing transition have been calculated by Albritten et al.<sup>16</sup> based on RKR potential curves. The results of this calculation have been plotted in Figure 7.

The apparent variation, for the most part, is a decrease in transition moment with increasing internuclear distance. However,

the results for the  $v' = 1$  level do not fit this pattern. One must conclude either that the variation is not a simple monotonic decrease, or that perhaps the  $\text{NO}^+(\text{A}^1\Pi_u)$  state is in fact populated to a significant extent by cascade transitions from higher-lying states.

#### ACKNOWLEDGEMENTS

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12. G. M. Lawrence, Phys. Rev. A. 2, 397 (1970).
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14. The excitation function is taken here to mean the number of photons detected per unit time per unit of electron beam current per unit of pressure in the collision chamber, as a function of electron energy. As such it is directly proportional to the total excitation cross section as a function of electron energy, including all

optically allowed cascade transitions.

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Table I

## Excitation Cross Sections for Observed Emission Features

Feature		$\lambda$ (Å)	$\sigma$ ( $10^{-18} \text{ cm}^2$ )	Electron energy
O I		1304	$1.14^a$	100 v.
NO <sup>+</sup> (A ← X)	(0, 0)	1368	$0.34 \pm .03^b$	"
	(0, 1)	1414	$1.17 \pm .05$	"
	(0, 2)	1461	$1.70 \pm .05$	"
	(0, 3)	1511	$1.71 \pm .05$	"
	(0, 4)	1565	$1.20 \pm .05$	"
	(0, 5)	1621	$0.60 \pm .04$	"
	(1, 0)	1340	$0.45 \pm .04$	"
	(1, 1)	1383	$0.81 \pm .04$	"
	(1, 2)	1428	$0.49 \pm .04$	"
	(1, 5)	1581	$0.26 \pm .03$	"
	(2, 0)	1313	$0.26 \pm .02$	"
	(3, 0)	1288	$0.09 \pm .01$	"
NO β'	(5, 0)	1524	$0.17 \pm .02$	25 v.
	(4, 0)	1549	$0.19 \pm .02$	"
NI		1200	$3.04 \pm .10$	100 v.
		1243	$0.74 \pm .04$	"
		1493	$1.26 \pm .05$	"

(TABLE I)

<sup>a</sup> This result is due to Lawrence (Reference 11) and is used as standard for all other cross sections given.

<sup>b</sup> Error estimates are based on the reproducibility of the data, and as such represent probable error relative to the cross section for the OI( $\lambda 1304\text{\AA}$ ) emission. The estimated probable error in absolute values is an additional  $\pm 20\%$ .

Table II

Relative Intensities in  $\text{NO}^+$  (A - X) Baer-Miescher Bands

	0	1	2	3	4	5
0	.050 1368.3	.167 1413.7	.261 1461.4	.256 1511.8	.176 1564.9	.091 1621.1
1	.212 1339.7	.385 1383.1	.232 1428.8	.024 1476.9	.027 1527.6	.120 1581.0
2	.398 1313.0	.337 1354.7	.022 1398.5	.068 1444.6	.136 1493.0	.039 1544.0
3	.580 1288.2	.165 1328.3	.038 1370.4	.161 1414.5	.025 1461.0	.032 1509.8
4	.651 1265.0	.021 1303.7	.163 1344.2	.053 1386.6	.023 1431.2	.089 1478.0
5	.659 1243.4	.014 1280.7	.205 1319.8	.000 1360.7	.100 1403.6	.022 1448.6

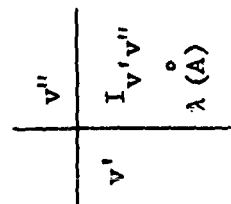


Table III  
Total Cross Sections for Selected Vibrational Levels of the  
 $\text{NO}^+(\text{A}^1\Pi_u)$  State<sup>†</sup>

	$\sigma(\text{Total})^*$
$v' = 0$	6.7 (-18) $\text{cm}^2$
1	2.12(-18) $\text{cm}^2$
2	0.66(-18) $\text{cm}^2$
3	1.55(-19) $\text{cm}^2$

\* at 100 eV.

<sup>†</sup> For process (9).

## Figure Captions

Figure 1 Diagram of the experimental apparatus.

Figure 2 Relative spectral response of the optical system. The ordinate, for each set of data, is the quotient of observed intensity divided by expected intensity. The solid line is a composite of least-squares third-order fits to the two sets of data.

Figure 3 Observed VUV spectrum of nitric oxide under impact of 100 eV electrons (histogram). Two bands of the NO  $\beta'$  band system are shown as they appeared at an excitation energy of 30 eV (dotted outlines). All other band ( $v'$ ,  $v''$ ) designations refer to the NO<sup>+</sup>(A - X) bands. The dashed line indicates the relative spectral sensitivity of the optical system.

Figure 4 Measured excitation functions for bands of the NO<sup>+</sup>(A - X) system and the NO  $\beta'$  system.

Figure 5 Measured total cross section for the dissociative excitation of NO to produce the  $\lambda 1200\text{\AA}$  emission of atomic nitrogen.

Figure 6 Variation in dipole transition moment for the NO<sup>+</sup>(A - X) band system.

Figure 7 Apparent variation in transition moment for the transition  
 $\text{NO}(^2\Pi_r) \rightarrow \text{NO}^+(A^1\Pi_u).$

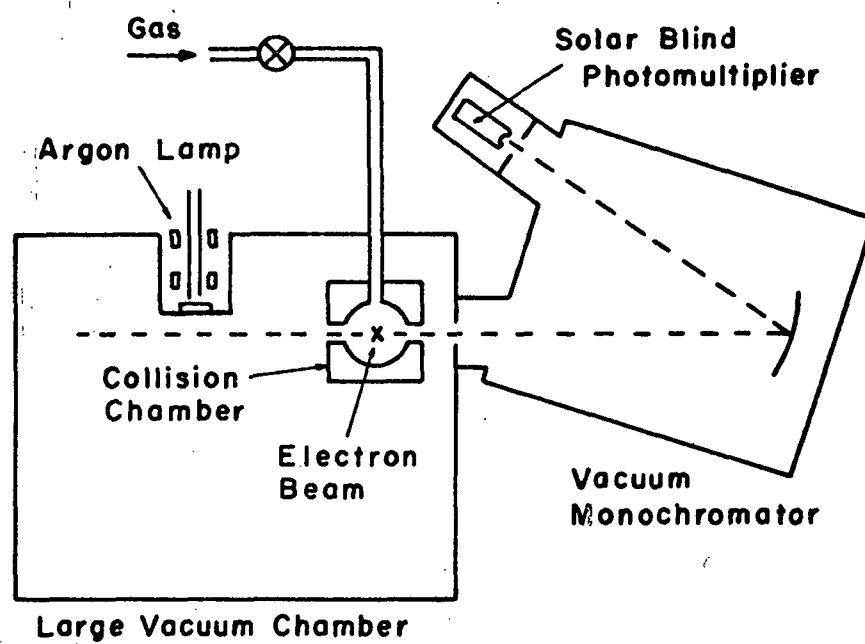


Figure 1

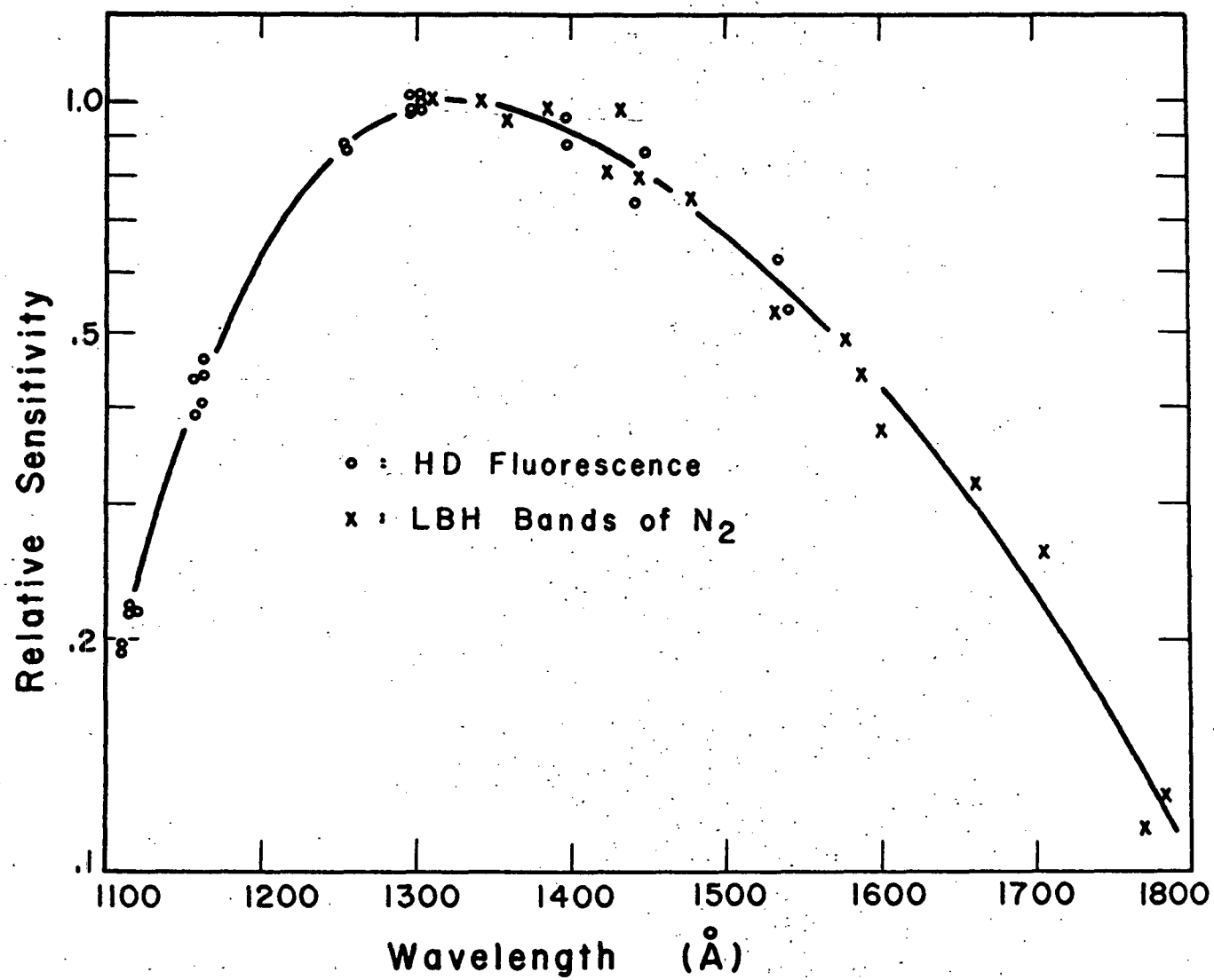


Figure 2

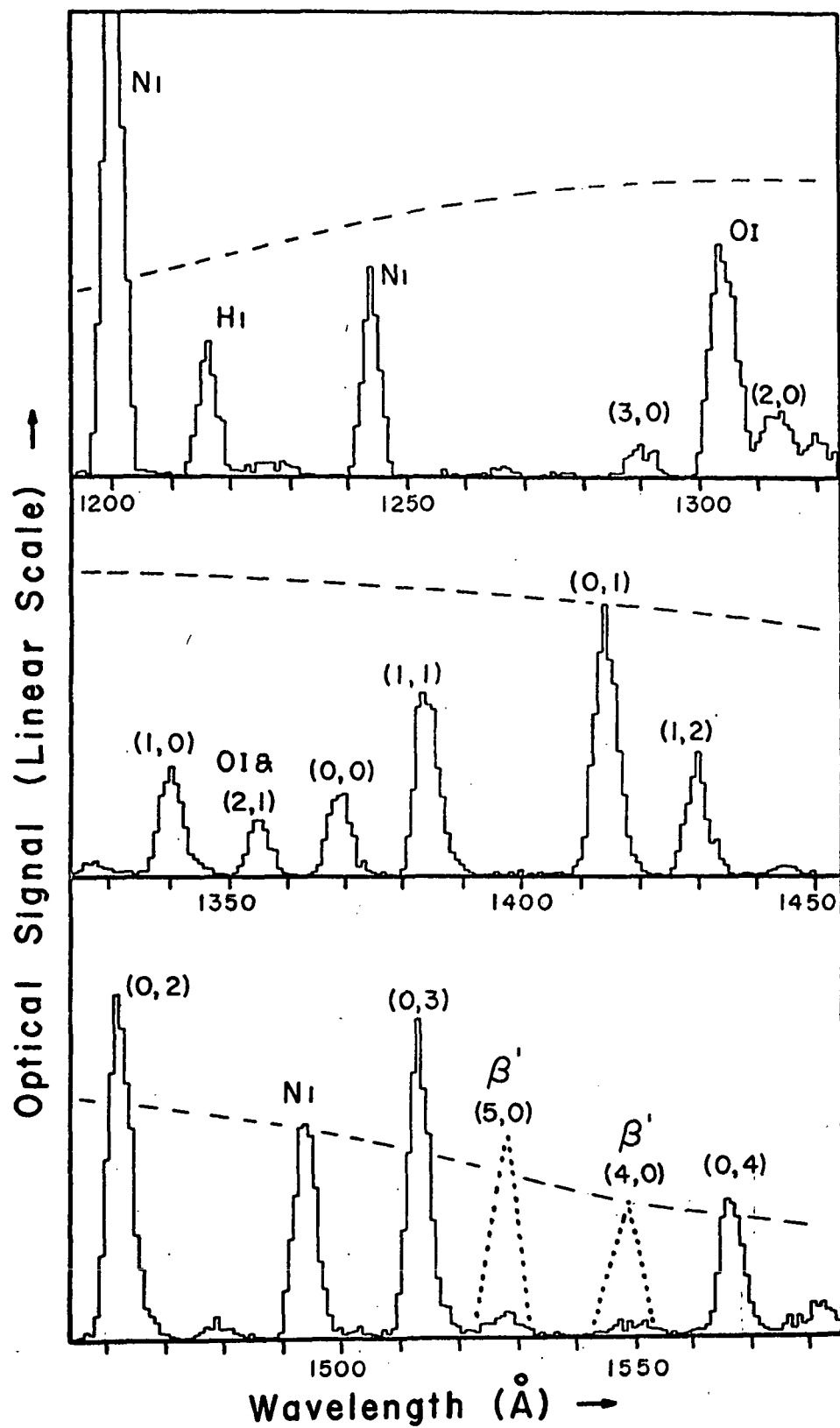


Figure 3



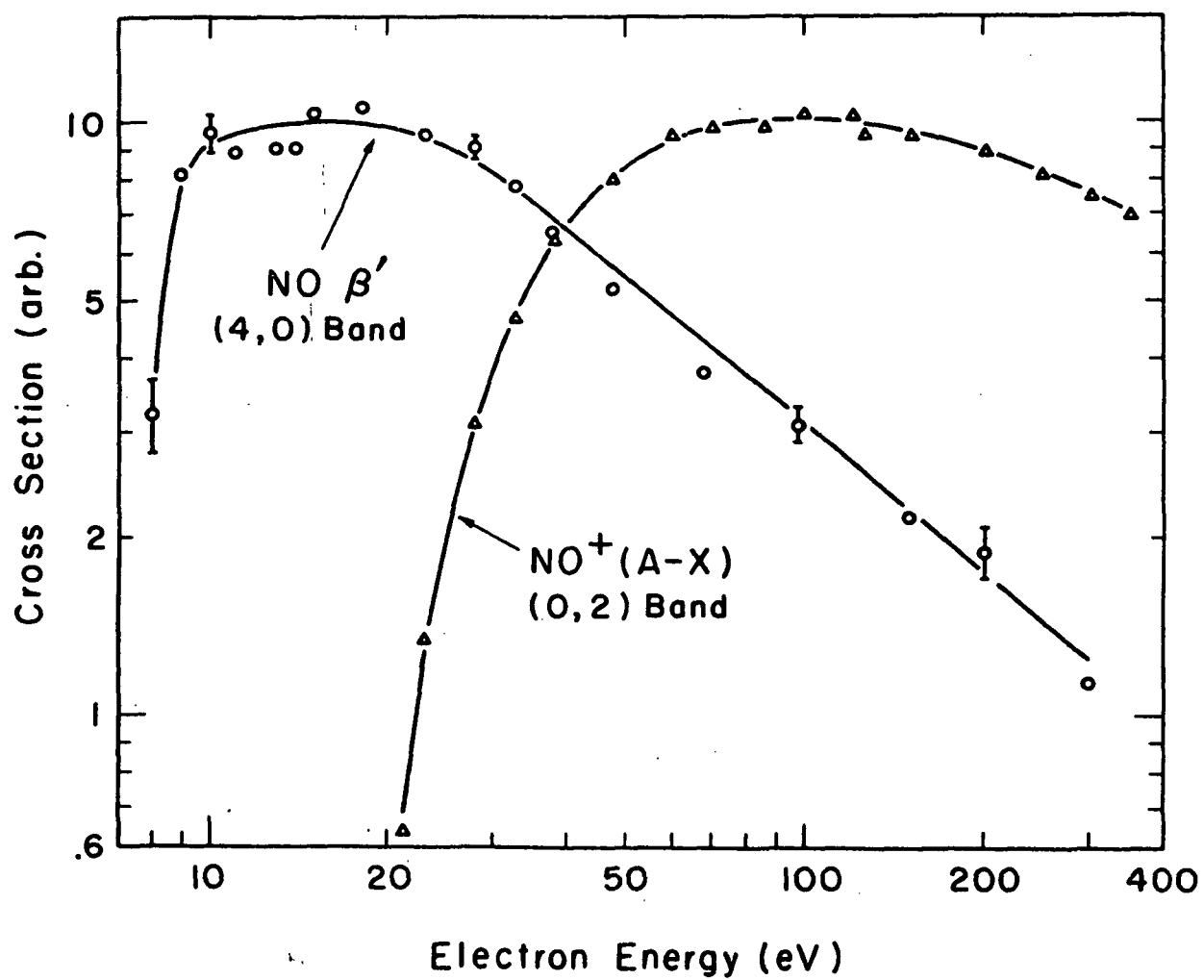


Figure 4

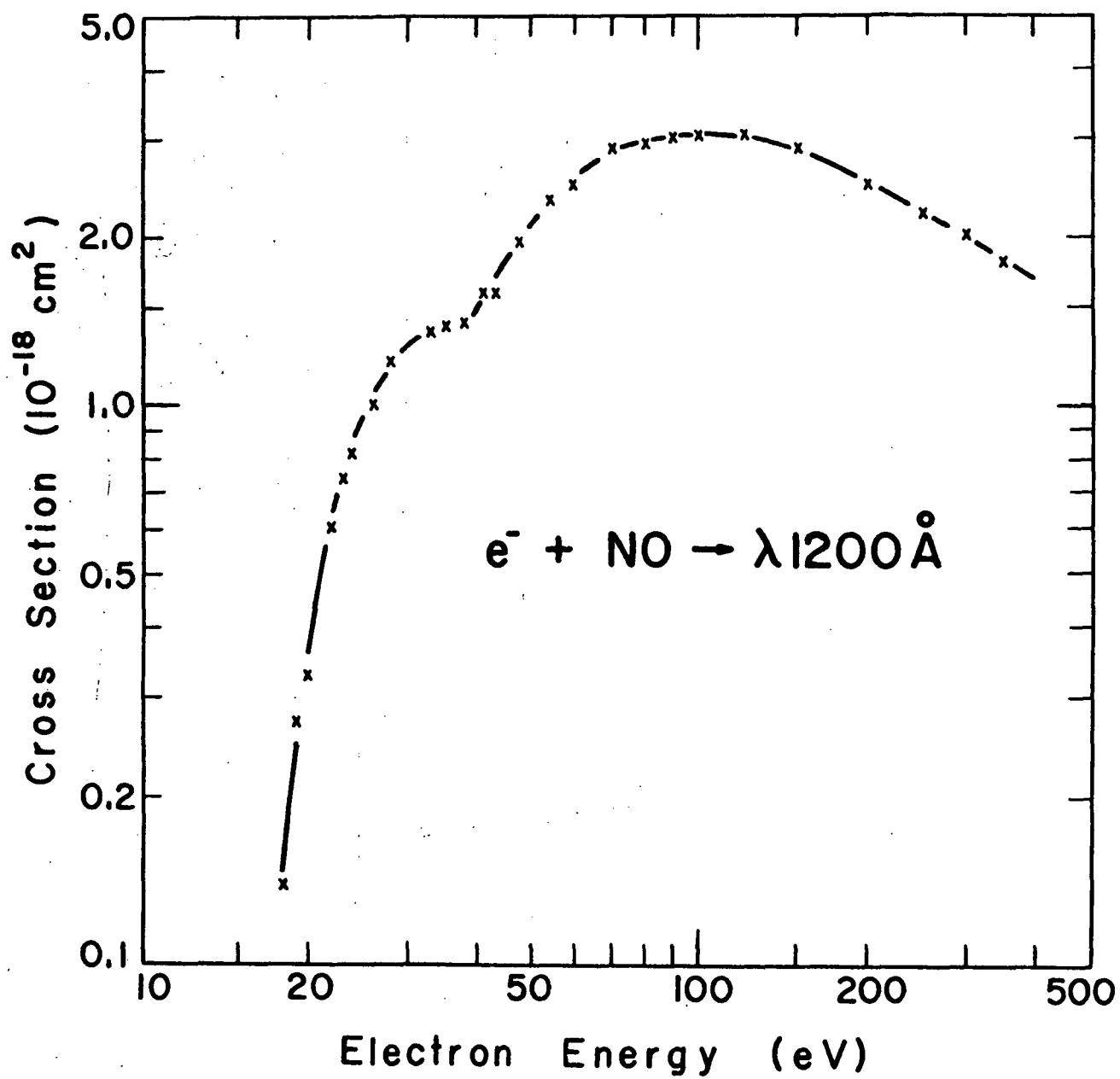


Figure 5

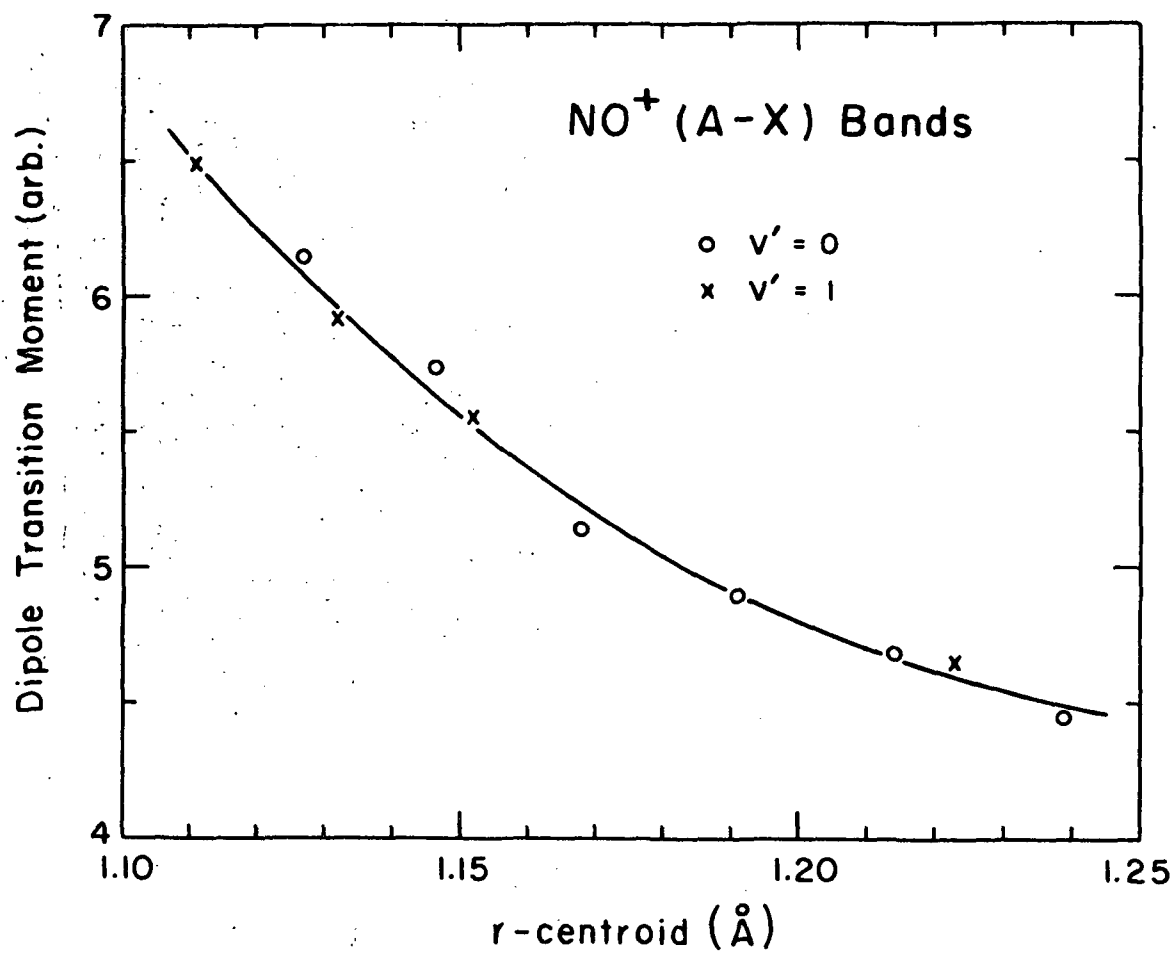


Figure 6

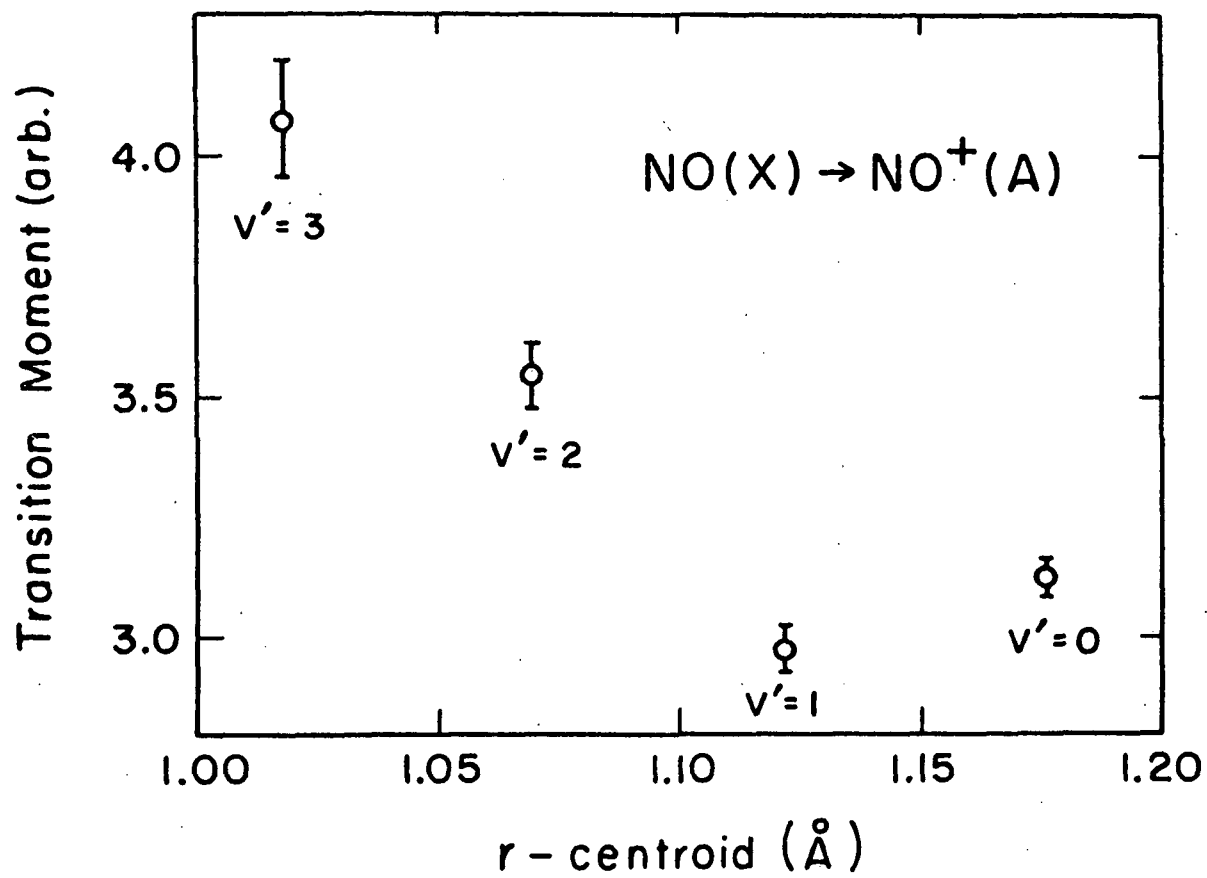


Figure 7