Electron impact excitation of the gamma bands of nitric oxide

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The excitation of several pronounced γ bands of NO by electron impact was studied from threshold to 1000 eV. A high optical efficiency was achieved by using an ellipsoidal collision chamber with mirrored interior surfaces. The interaction volume viewed was located at one of the foci of the ellipsoid. A 0.25 m double monochromator and single photon counting techniques were employed to monitor molecular band intensities. The optical sensitivity between 2000 and 4000 Å was obtained with the molecular branching ratio method by monitoring $1NG\ CO^+$, $1NG\ N_2^+$, $2PG\ N_2$ band intensities and suitable progressions in the γ system of NO. Second order effects were avoided by low NO densities ($\sim 10^{-4}$ torr) in the collision chamber. No ionization gauges were used during measurement, thus eliminating the possible dissociation of NO and subsequent formation of N_2. Absolute cross sections for γ bands were obtained by normalizing to the $2PG(0,0)$ band of N_2. For this purpose, a known mixture of NO and N_2 was prepared in a gas handling manifold using a manometer. For the unambiguously identifiable (0,1), (0,2), (1,0), (1,5), and (2,7) γ bands of NO, the cross sections peaked near 18 eV and had values of 2.2, 1.8, 6.3, 1.3, and 0.57×10^{-19} cm^2, respectively, with a possible error of 25%. The relative peak cross sections agree with calculated band intensities within 20%.

I. INTRODUCTION

Nitric oxide seems to occur in rather large concentrations in the disturbed atmosphere under auroral conditions.[1,2] A study of the electron impact excitation of this molecule may, therefore, be of interest in upper atmospheric modeling.

The present work is concerned with the measurement of absolute cross sections for the excitation of the relatively intense and identifiable (0, 1), (0, 2), (1, 0), (1, 5), and (2, 7) bands of the γ system of NO from threshold to 1000 eV.

Some data exists on relative electron impact cross sections of the γ system ($A\,^2\Sigma^+ \rightarrow X\,^2\pi$) and the β system ($B\,^2\pi \rightarrow X\,^2\pi$) of NO.[3,4] The lack of more extensive information may be due to experimental difficulties such as problems with availability of pure NO, appreciable thermal dissociation on hot filament surfaces, attenuation of radiation due to resonance absorption, and the relative smallness of the excitation cross sections involved. It was attempted in the present work to avoid these problems where possible and thus obtain the first measurement of absolute excitation cross sections for the γ bands of NO.

II. EXPERIMENTAL DETAILS AND METHOD

The experimental arrangement was similar to that described in our previous work[5,6] except for a change in the diffraction gratings (now 1200 grooves/mm blazed at 3000 Å) of the double monochromator. Figure 1 shows the geometry of the electron beam and the optical lenses in the ellipsoidal collision chamber for the most efficient collection of the emitted photons. A diffuse gas source was used and the pressure in the collision chamber was kept in the 10^{-4} torr range during the experiment. The electron beam current varied from a fraction of 1 to 50 μA.

A. Pressure calibration

To eliminate the effect of the dissociation of NO by the hot cathode of the pressure gauge on the count rates, the approximate pressure in the collision chamber was obtained by measuring the pressure in the vacuum enclosure and taking into account the various conductances in the system. In order to avoid uncertainties in the precise determination of the NO density in the collision chamber and in the effective interaction volume viewed by the optical system, the count rates of the γ bands of NO were compared with those for the $2PG(0, 0)$ band of N_2, for which the cross section is well known.[5] A 1 : 1 mixture of NO and N_2 was prepared as follows.

Nitrogen from a 1 liter flask was admitted into the gas handling manifold and the gas pressure in the manifold was measured with a manometer (Matheson 63-5601). The N_2 flask was then closed after attaining the equilibrium density of the entire manifold. The manifold was then evacuated. Nitric oxide from a Matheson lecture bottle (with about 2% N_2 impurity) was let into the evacuated manifold which had another previously evacuated 1.0 liter flask connected to it. This flask was filled

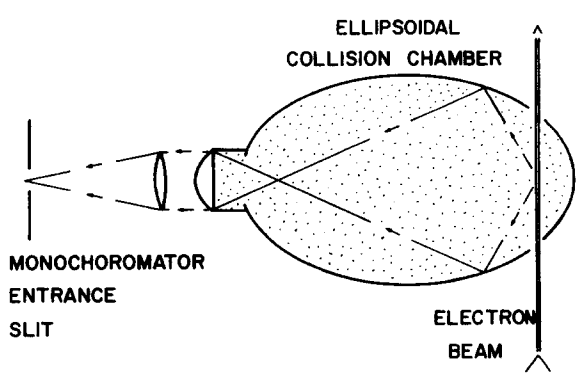

FIG. 1. Simplified schematic diagram of the ellipsoidal collision chamber and optical system.

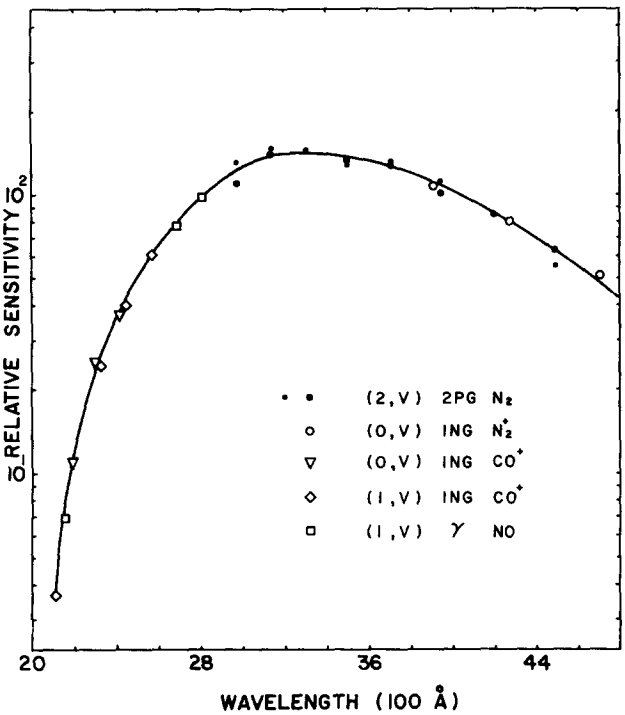

FIG. 2. Relative sensitivity of the optical system as a function of wavelength obtained with the molecular-branching-ratio technique. For the $2PG(2, v'')$ progression of N_2, both calculated (•) and experimental (○) relative cross sections were used.

with NO gas to the same equilibrium density of the entire manifold as in the case of N_2. The NO flask was then closed and the manifold was again evacuated. Finally, N_2 and NO gases were admitted into the manifold from these two flasks thus establishing a calibrated 1 : 1 mixture of NO and N_2.

B. Cross section determination

By comparing intensities of NO and N_2 bands, the cross sections for γ bands were obtained from

$$\sigma_{\gamma,\mathrm{NO}} = \sigma_{N_2} \frac{C_{\gamma,\mathrm{NO}}}{C_{N_2}} \frac{K_{N_2}}{K_{\gamma,\mathrm{NO}}} \frac{N_{N_2}}{N_{\mathrm{NO}}} \frac{T_{N_2}}{T_{\gamma,\mathrm{NO}}}, \quad (1)$$

where σ is the absolute cross section, C the count rate, K the relative sensitivity of the optical system, which is a function of wavelength and geometry, N the number density, and T the effective transmission of the monochromator for the band in question. The absolute cross section σ_{N_2} in Eq. (1) was taken as that for the $2PG(0, 0)$ band of N_2 at 3371 Å. A value of $1.05(10)^{-18}$ cm^2 was assumed at an energy of 40 eV.[5] Values for K were obtained from Fig. 2 (see below). The number densities N_{N_2} and N_{NO} were made equal by preparing a gas mixture as described above.

The effective transmission (T) of the monochromator for the γ bands of NO were assumed to be equal to that for the $2PG(0, 0)$ band of N_2. This assumption was verified by varying the slit widths of the monochromator and monitoring the resulting intensity. The possible error associated with this assumption is about 10%.

C. Optical calibration

Calibration of the spectral response of the optical system in the region between 2000 and 4000 Å was accomplished using the molecular-branching-ratio technique (see also Table I)[11] as follows.

Spectra of N_2, NO, and CO^+ were obtained in separate

TABLE I. Relative cross sections used to obtain the relative sensitivity of the optical system.

Progression	Reference Exptl	Reference Theor	Band	Wavelength (Å)	Relative count rate (this work)	Relative cross section Exptl	Relative cross section calc. [Eq. (2)]
$2PG$ $(2, v)$ of N_2	7	9	(2, 0)	2976	0.190	0.78	0.659
			(2, 1)	3136	0.575	1.90	1.669
			(2, 2)	3309	0.038		0.111
			(2, 3)	3500	0.083	0.29	0.276
			(2, 4)	3710	0.200	0.73	0.637
			(2, 5)	3943	0.130	0.60	0.497
			(2, 6)	4200	0.050	0.27	0.249
			(2, 7)	4490	0.013	0.096	0.099
$1NG$ $(0, v)$ of N_2^+	8		(0, 0)	3914	16.500	1.000	
			(0, 1)	4278	3.900	0.32	
			(0, 2)	4709	0.470	0.06	
$1NG$ $(0, v)$ of CO^+		10	(0, 0)	2190	1.317		0.500
			(0, 1)	2300	1.615		0.269
			(0, 2)	2419	0.625		0.070
$1NG$ $(1, v)$ of CO^+		10	(1, 0)	2112	0.122		0.198
			(1, 2)	2325	0.630		0.150
			(1, 3)	2446	0.567		0.085
			(1, 4)	2578	0.242		0.023
γ $(1, v)$ of NO		10	(1, 0)	2151	1.340		0.500
			(1, 5)	2675	3.000		0.101
			(1, 6)	2805	2.450		0.065

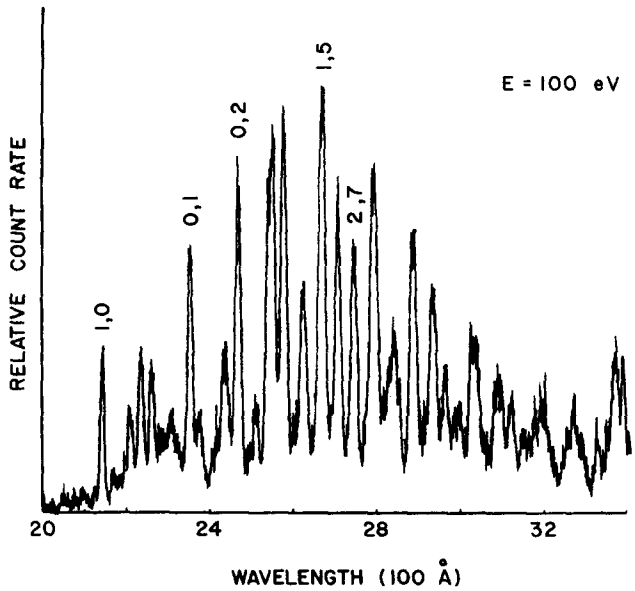

FIG. 3. A typical NO spectrum excited at 100 eV electron energy. The γ bands studied are labeled.

runs. By choosing bands belonging to the same progression with the same upper vibrational level v', the relative intensities did not depend on electron energy and cascade effects were eliminated. These intensities were compared with experimental and/or calculated relative cross sections (Table I) to find the relative spectral response of the optical system. The results for the different progressions used were normalized near 3200 Å to obtain a smooth continuous curve (Fig. 2) that represented the relative sensitivity of the optical system in the desired wavelength region.

The relative cross sections used in the optical calibration were calculated from the expression

$$\sigma_{v'v''} \propto q_{0v'} q_{v'v''} \nu_{v'v''}^3 \frac{|R_{v'v''}|^2}{\Sigma_{v''} A_{v'v''}}, \tag{2}$$

where $\sigma_{v'v''}$ is the relative cross section and $q_{v'v''}$ the Franck–Condon factor for the band in question, $q_{0v'}$ the Franck–Condon factor for the transition from the $v=0$ level of the ground electronic state to the v' level of the upper electronic state from which the bands originate, $\nu_{v'v''}$ the frequency of the transition (band head), $R_{v'v''}$ the electronic dipole moment (assumed to be constant for a given v' progression), and $A_{v'v''}$ the Einstein coefficient ($\Sigma_{v''} A_{v'v''}$ is a constant for a given v' progression). The values of q and ν for the various gases used were taken from the references shown in Table I. The use of the $\gamma(1, v'')$ progression of NO in Fig. 2 was to confirm the consistency with the $1NG$ CO^+ data in the region below 3000 Å.

III. RESULTS AND DISCUSSION

A spectrum of NO excited at an electron energy of 100 eV is shown in Fig. 3. The identifiable γ bands studied in this work are labeled in this figure. The absolute cross sections for these bands as a function of electron energy are shown in Fig. 4. These cross sections are also listed in Table II. The error bars in Fig. 4 show the variations of the data in repeated runs. The possible error in the absolute cross sections is comprised of uncertainties in the transmission of the optical monochromator (10%), optical sensitivity (10%), mixture of NO and N_2 (5%), and absolute cross section for the $2PG(0,0)$ band of N_2 (10%). This results in a probable error in the cross sections of about 20 to 25%. The over-all variation of the cross sections as a function of energy is that expected for electronically allowed transitions.

TABLE II. Absolute cross sections for some γ bands of NO.

	Cross section ($cm^2 \times 10^{-19}$)				
Energy (eV)	(0,1) 2366 Å	(0,2) 2474 Å	(1,0) 2151 Å	(1,5) 2675 Å	(2,7) 2759 Å
6		0.34	0.4	0.10	
7	0.76	0.70	3.2	0.63	0.22
8	1.16	0.95	4.4	0.82	0.35
9	1.41	1.14	5.1	0.96	0.43
10	1.60	1.30	5.6	1.05	0.48
12	1.85	1.50	6.2	1.18	0.54
14	2.00	1.61	6.3	1.23	0.56
16	2.10	1.70	6.3	1.28	0.58
18	2.13	1.73	6.2	1.29	0.58
20	2.16	1.76	6.0	1.29	0.57
25	2.12	1.73	5.6	1.24	0.55
30	2.03	1.67	5.2	1.19	0.52
40	1.88	1.52	4.5	1.07	0.48
50	1.73	1.40	4.0	0.98	0.45
60	1.60	1.29	3.6	0.89	0.42
80	1.40	1.11	3.0	0.77	0.37
100	1.24	1.00	2.6	0.68	0.34
200	0.84	0.67	1.63	0.46	0.24
400	0.55	0.43	1.00	0.31	0.17
700	0.39	0.30	0.67	0.22	0.13
1000	0.31	0.24	0.52	0.18	0.10

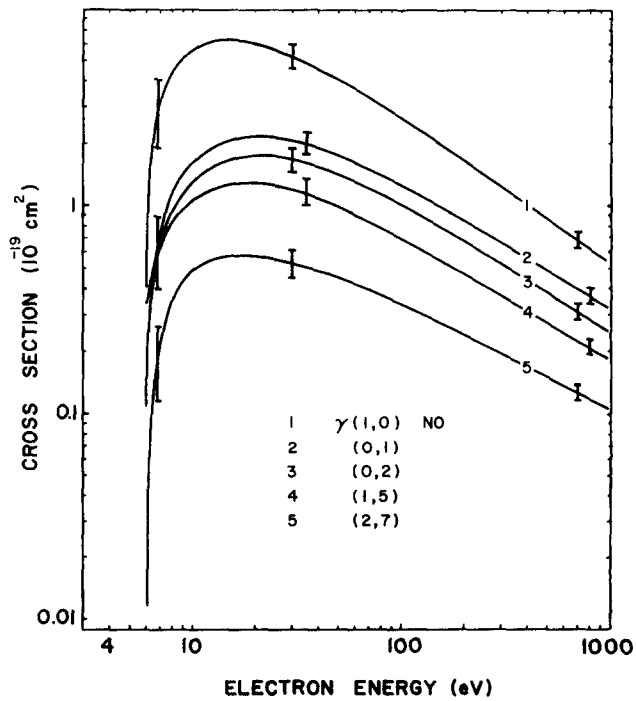

FIG. 4. Absolute cross sections for several pronounced γ bands of NO as function of the electron impact energy. The error bars show the variation of data points in repeated runs.

TABLE III. A comparison of absolute cross sections with calculated relative intensities for γ bands of NO.

γ band	Calculated relative intensity	Experimental cross section at 20 eV (10^{-19} cm^2)	Normalized
(0, 1)	317.7	2.16	360.0
(0, 2)	249.4	1.76	293.3
(1, 0)	1000.0	6.00	1000.0
(1, 5)	206.8	1.29	215.0
(2, 7)	122.0	0.566	94.3
Ratio of	Ratio of		Ratio of
(0, 1)/(0, 2)	1.27		1.23
(1, 0)/(1, 5)	4.83		4.65
(1, 0)/(0, 2)	4.01		3.41
(2, 7)/(1, 0)	0.122		0.094
(2, 7)/(0, 2)	0.489		0.322

The measured and calculated relative cross sections (band intensities) for γ bands are compared in Table III. While there is a good agreement in the cross section ratios of bands from the same progression, the ratios for bands from different progressions show greater differences. This may be due to the effect of cascade contributions in the case of bands with different upper vibrational levels.

The present results differ substantially from the work of Povch *et al.*,[4] whose relative cross section for the (1, 5) γ band of NO increases with electron energy to a maximum at about 170 eV, and has some structure below 18 eV energy. The maximum cross section for various γ bands of NO studied in this work occurs at about 18 eV, and no structure below 18 eV energy could be discerned within the statistical fluctuations of the data.

The polarization of the γ bands could not be studied explicitly in the present work. Indications exist, however, that the systematic error in the cross sections due to polarization effects was small and probably less than 10%. The reasons for this are as follows: General agreement exists between the experimental and theoretical results (Table III) for the γ bands studied. Therefore it seems, that polarization effects must have been small, especially in view of the other experimental uncertainties involved. Furthermore, the relative sensitivities for γ bands from a given progression followed a smooth curve, as is evident from Fig. 2 for the particular case of the $(1, v)$ progression. This again points to the smallness of polarization effects.

Even in the case that all bands studied had the same polarization, the resulting systematic error should have been rather small. Data obtained from the manufacturer of the diffraction gratings used show, that the grating efficiency varied by less than 5% for the two planes of polarization as compared to unpolarized light over the wavelength range of interest. The blaze wavelength chosen minimized the difference in signal response for both planes of polarization in this wavelength range.

It should be noted, however, that significant degrees of polarization may exist for the individual rotational lines of the γ bands.[12] Unfortunately, the limited dispersion of the monochromator used and small signal intensities did not permit a study of rotational lines in the present work. Only total band intensities could be monitored and for these, polarization effects seem to have been small.

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