

## LETTERS TO THE EDITOR

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## COMMUNICATIONS

# Doublet→quartet transitions in nitric oxide as detected by electron-impact spectroscopy<sup>a)</sup>

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We have detected and assigned vibronic bands belonging to the  $X^2\Pi \rightarrow a^4\Pi$  and  $X^2\Pi \rightarrow b^4\Sigma^-$  transitions in nitric oxide by the technique of low-energy, variable-angle, electron-impact spectroscopy. This represents the first direct observation of doublet→quartet excitations in the spectrum of nitric oxide and to our knowledge is the only example of doublet→quartet transitions observed in the gas phase.

While the doublet excited state spectrum of nitric oxide is rather well understood,<sup>1-4</sup> information on the doublet→quartet transitions is scarce. Previous studies<sup>5,6</sup> have reported emission bands from nitric oxide in rare gas matrices which were assigned as  $a^4\Pi v=0 \rightarrow X^2\Pi v'=n$  transitions (*M* bands). In addition, infrared emission bands from nitric oxide subjected to an electric discharge in a flow tube have been tentatively interpreted as resulting from  $b^4\Sigma^- \rightarrow a^4\Pi$  fluorescence.<sup>7,8</sup> Bernstein and Herzberg<sup>9</sup> were unable to optically observe the  $X^2\Pi \rightarrow a^4\Pi$  excitation using a 28 matm path.

In view of the sparsity of information about the quartet systems of this experimentally and theoretically important molecule, we used the technique of low-energy, variable-angle, electron-impact spectroscopy to investigate its electronic spectrum. Electron-impact spectroscopy has been shown to be well suited for the investigation of both spin- and symmetry-forbidden transitions.<sup>10,11</sup> The experimental apparatus has been described previously.<sup>10</sup> We report transitions observed in the 5 to 7.4 eV energy-loss region, which was studied at impact energies of 25, 35, and 50 eV, over scattering angles from 5° to 80°. Sample pressures were typically 1.8 mtorr while the incident electron beam current was approximately 70 nA. The energy resolution, as measured by the full width at half maximum of the elastic peak was set at about 0.085 eV.

Figure 1 shows the spectrum of nitric oxide at both low (20°) and high (80°) scattering angles. The low-angle spectrum results predominantly from spin-allowed,

TABLE I.  $X^2\Pi v=0 \rightarrow$  quartet excitation energies in the 5 to 7.4 eV region.

Excitation energy (eV)			Excitation energy (eV)		
Present observations ( $\pm 0.02$ eV)	Estimations from optical data	Present quartet assignment	Present observations ( $\pm 0.02$ eV)	Estimations from optical data	Present quartet assignment
5.22	(5.19) <sup>a</sup>	$a^4\Pi v'=4$	6.29	(6.28) <sup>d</sup>	$v'=4$
5.31	(5.30) <sup>a</sup>	5	6.43	(6.43) <sup>d</sup>	5
5.41	(5.41) <sup>a</sup>	6	6.57		6
5.55 <sup>b</sup>	(5.51) <sup>a</sup>	7	6.70		7
5.60	(5.60) <sup>a</sup>	8	6.83		8
5.70	(5.70)	$b^4\Sigma^- v'=0^c$	6.97		9
5.86		1	7.12		10 <sup>e</sup>
6.00	(5.99) <sup>d</sup>	2	7.24		11 <sup>e</sup>
6.14	(6.15) <sup>d</sup>	3	7.36		

<sup>a</sup>Estimated transition energies based on rare gas matrix optical emission data; Ref. 6.

<sup>b</sup>Energy uncertainty  $\pm 0.05$  eV.

<sup>c</sup>The upper state is predominantly  $b^4\Sigma^- v'=0$  with a small  $a^4\Pi v'=9$  contribution. The latter is also estimated in Ref. 6 to occur at 5.70 eV.

<sup>d</sup>Transition energy estimates using the optical data of Refs. 6 and 7 and the present assignments.

<sup>e</sup>Assignment uncertain.

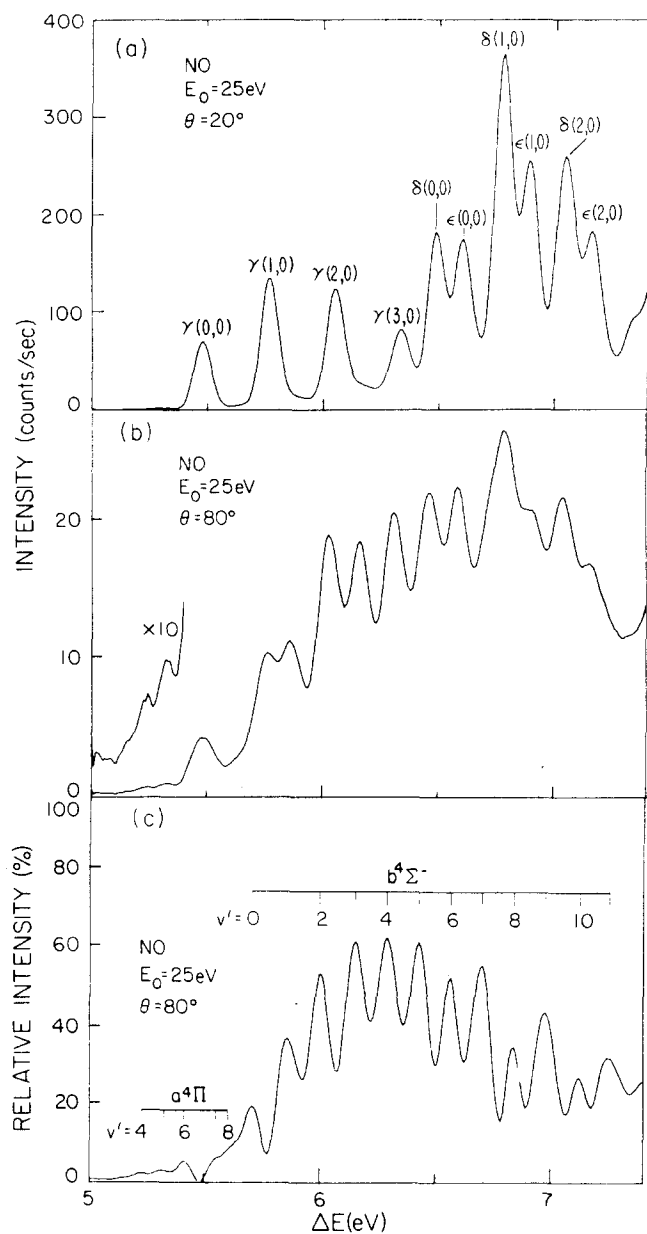


FIG. 1. Electron energy-loss spectrum of nitric oxide at scattering angles (a)  $20^\circ$  and (b)  $80^\circ$ , at an impact energy of 25 eV. Total scanning times were (a) 360 min and (b) 760 min. (c) Shows the resulting difference spectrum of (b) minus (a), the latter having been scaled so as to make the reference peak at 5.47 eV (due to the  $X^2\Pi v=0 \rightarrow A^2\Sigma^+ v'=0$  excitation) in the difference spectrum vanish. The ordinate in (c) is expressed as a fraction of the most intense feature of (b). In panel (a), the bands designated  $\gamma$ ,  $\delta$ ,  $\epsilon$  belong to the transitions  $X^2\Pi \rightarrow A^2\Sigma^+$ ,  $C^2\Pi$ , and  $D^2\Sigma^+$ , respectively, and the two numbers in parentheses designate the final and initial vibrational states, in that order.

doublet-doublet transitions and is found to be in good agreement with previous optical studies.<sup>1-4</sup> In the electron-impact spectrum at high scattering angles, the intensity of spin-forbidden transitions relative to spin-allowed transitions is in general one to two orders of magnitude greater than at low angles.<sup>10,11</sup> The significant changes in the spectra in going from  $20^\circ$  to  $80^\circ$  are

the result of this fact. In order to extract the maximum amount of information from these changes, the  $20^\circ$  spectrum, appropriately scaled (see Fig. 1 caption), has been subtracted from the  $80^\circ$  spectrum.<sup>11(a),12</sup> The difference spectrum [Fig. 1(c)] is primarily the result of doublet-quartet transitions. The application of this difference technique requires high signal-to-noise ratios, sufficient resolution, and therefore relatively long scanning times. Doublet-quartet excitations contribute a maximum of nearly 60% of the total intensity of the  $80^\circ$  spectrum. Similar subtractions have been performed using as the high-angle spectrum data taken at  $40^\circ$  and  $60^\circ$ . Also, subtractions were performed using a different reference peak [ $\delta(2,0)$ ] and spectra taken at 50 eV impact energy. All difference spectra thus obtained are substantially the same.

We have assigned the transitions shown in the subtraction spectrum to vibronic elements of the  $X^2\Pi \rightarrow a^4\Pi$  and  $X^2\Pi \rightarrow b^4\Sigma^-$  excitations. These assignments are based on the angular behavior of the observed transitions which identifies the excitations as spin-forbidden<sup>10,11</sup> and on semiempirical theoretical calculations<sup>13</sup> of the  $a^4\Pi$  and  $b^4\Sigma^-$  excitation energies. In addition, the locations of some quartet vibronic bands may be predicted from the previous limited optical experimental results. Observed transition energies, predicted energies, and assignments are summarized in Table I. A more detailed description of the nitric oxide spectrum will be forthcoming.

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