# On the Photoelectron Spectrum of NO

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The photoelectron spectra of NO have been remeasured with 584 Å and 304 Å He lines at high resolution and the energies of the bands have been determined by calibration against argon. A weak He I line 320.4 Å has been found to cause the small peak at 20.4 eV, which was assigned earlier as the $c\,^3\Pi$ state. The $c\,^3\Pi$ and $B\,^1\Pi$ states have nearly the same energy, 21.7 eV. The vibrational structure of the $B'\,^1\Sigma^+$ state at 22.5 eV has been resolved.

## Introduction

The photoelectron spectrum of NO has been studied by us earlier [1]. Since then our apparatus has been improved with respect to resolution, intensity and stability. A short description was given in connection with our work [2] on $O_2$. As we observed anomalous intensity ratios concerning especially the state $c\,^3\Pi$ we have carefully remeasured the whole spectrum, both with the 584 Å and 304 Å He lines.

The electronic structure of $NO^+$ is well understood with the exception of the higher states above 20 eV, where some uncertainty still exists. Quantum-mechanical calculations on NO have been made recently by LEFEBVRE-BRION [3]. It is also possible to compare the calculations on CO by O'NEIL and SCHAEFER [4] with the $NO^+$ ion, as CO and $NO^+$ are isoelectronic.

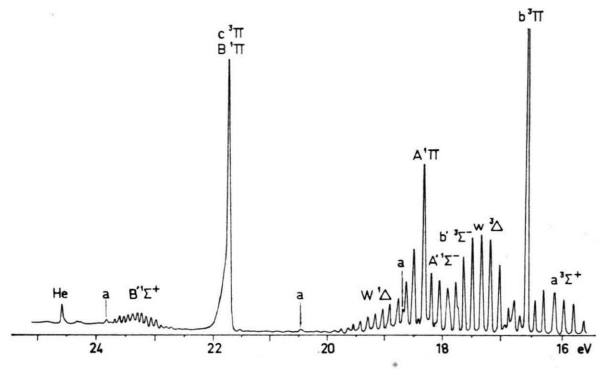


Fig. 1. Photoelectron spectrum of NO using the He 304 Å line. Three small peaks marked with *a* are due to the He 320 Å line. Recording time was 75 hours.

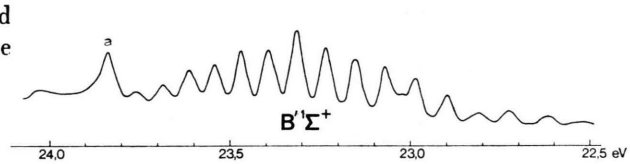


Fig. 2. Photoelectron spectrum of the $B'\,^1\Sigma^+$ state with 304 Å light. The peak at *a* is due to 320 Å light.

## Results

The 304 Å spectrum of $NO^+$ has been measured with a resolution of 25 meV, Fig. 1. The vibrational structure of the progression at 23 eV is resolved, Fig. 2. The large peak at 21.7 eV exhibits a partially resolved structure, Fig. 3. Energies and intensities of the bands, determined within $\pm 10$ meV, are given in Table 1.

A careful investigation of the spectral bands from the He light source has shown that beside the main He I and He II line systems there is a transition from the doubly excited level $2p^2\,^3P$ to $1s2p\,^3P^0$ corresponding to 38.697 eV or 320.399 Å. This line gives three visible "ghost" peaks at 18.7 eV, 20.4 eV, and 23.8 eV (see Fig. 1). In our former paper [1] the peak 20.4 eV was wrongly interpreted as a new state $c\,^3\Pi$, but it is in fact the $A\,^1\Pi$ state observed with the 320 Å line.

The 584 Å spectrum has been measured with 10 meV resolution, which makes it possible to observe the spin-orbit coupling. Part of the spectrum is shown in Fig. 4. Table 2 gives the position of the vibrational bands measured at the "midpoint" of the

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[1] O. EDQVIST, E. LINDHOLM, L. E. SELIN, H. SJÖGREN, and L. ÅSBRINK, Ark. Fys. **40**, 439 [1970].

[2] O. EDQVIST, E. LINDHOLM, L. E. SELIN, and L. ÅSBRINK, Phys. Scripta **1**, 25 [1970].

[3] H. LEFEBVRE-BRION, Chem. Phys. Lett. **9**, 463 [1971].

[4] S. V. O'NEIL and H. F. SCHAEFER III, J. Chem. Phys. **53**, 3994 [1970].

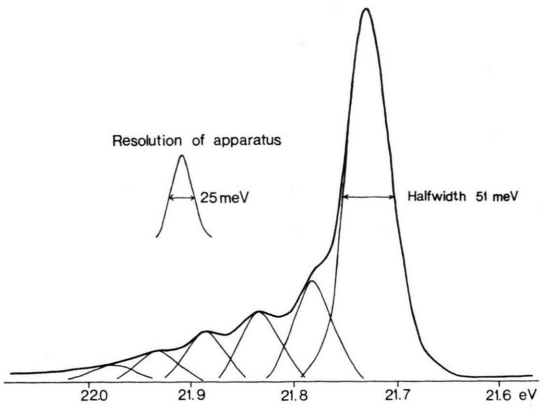


Fig. 3. c $^3\Pi$ and B $^1\Pi$ states in the photoelectron spectrum of $NO^+$ with 304 Å light. The deconvolution of the band is shown with weak lines.

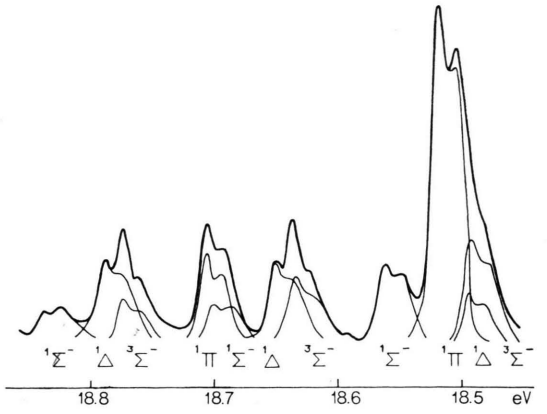


Fig. 4. Photoelectron spectrum of NO with 584 Å light. Resolution 10 meV. Deconvolution of the peaks is drawn with weak lines.

Table 1. States of $NO^+$, measured with 304 Å.

| State | $v$ | Energy midpoint (eV) | Intensity arbitrary units | Half-width (meV) | Diff. |
|---|---|---|---|---|---|
| c $^3\Pi$ | 0 | 21.722 | 805 | 51 | |
| and B $^1\Pi$ | | $21.77_9$ | 175 | ~ 44 | |
| | | $21.83_0$ | 109 | ~ 44 | |
| | | $21.88_4$ | 78 | ~ 44 | |
| | | $21.93_0$ | 45 | ~ 44 | |
| | | 21.97 | 22 | | |
| B′ $^1\Sigma^+$ | 0 | 22.727 | 6 | 40 | |
| | 1 | 22.811 | 3 | 40 | 84 |
| | 2 | 22.897 | 10 | 36 | 86 |
| | 3 | 22.987 | 15 ? | | 90 |
| | 4 | 23.069 | 18 ? | | 82 |
| | 5 | 23.152 | 22 | 37 | 83 |
| | 6 | 23.233 | 23 | 34 | 81 |
| | 7 | 23.313 | 29 | 38 | 80 |
| | 8 | 23.392 | 20 | 38 | 79 |
| | 9 | 23.468 | 16 | 32 | 76 |
| | 10 | 23.542 | 12 | 33 | 74 |
| | 11 | 23.613 | 12 | 37 | 71 |
| | 12 | 23.684 | 5 | 33 | 71 |
| | 13 | 23.756 | 3 | | |
| Other peaks | | 20.434 | 15 | A $^1\Pi$ with 320.4 Å | |
| | | 23.838 | 45 | c $^3\Pi$ and B $^1\Pi$ with 320.4 Å | |
| | | 18.677 | | b $^3\Pi$ with 320.4 Å | |
| | | $21.53_2$ | 6 | | |
| | | $22.23_7$ | 6 | | |
| | | $22.43_1$ | 4 | | |
| | | $22.52_7$ | 2 | | |
| | | 22.619 | 6 | 38 | |
| | | 23.02 | 10 ? | Uncertain | |
| | | 24.03 | 4 ? | Uncertain | |
| | | $24.25_3$ | 7 | | |
| | | $24.30_7$ | 10 | | |
| | | 24.587 | 57 | He | |

peak at its half height. The energy of the highest band peak and the spin-orbit coupling constant are also given. We estimate the energy to be correct within $\pm 3$ meV. The stability of the measurements was checked by repeated calibrations against the 15.7598 eV argon line and the drift, which was less than 3 meV, has been corrected for.

The new 584 Å measurements seem to confirm our previous analysis, but some energies should be slightly adjusted. The numbering of W $^1\Delta$ is still uncertain, as the beginning of the progression is completely overlapped.

## The c $^3\Pi$, B $^1\Pi$, and B′ $^1\Sigma^+$ States of $NO^+$

In the region 20 – 26 eV we expect the two $\Pi$-states c $^3\Pi$ and B $^1\Pi$ and the B′ $^1\Sigma^+$ state, but we find only two separate bands.

The assignment of the band at 23.6 eV as B′ $^1\Sigma^+$ is strongly supported by the vibrational structure, the intensity and by a comparison with the isoelectronic molecules CO and $N_2$ (cf. [1]). Quantum mechanical calculations [4] on CO and experimental results [5] on $N_2$ show the $^1\Sigma^+$ state to lie about 12.0 respectively 12.85 eV above the ground state, which for $NO^+$ should correspond to an energy of about 22 eV. The vibrational energy, $\sim 700$ cm$^{-1}$, is very low which is the case also in $N_2$ and CO.

The B′ $^1\Sigma^+$ band system is completely resolved. The vibrational structure is comparatively regular (Fig. 2), but the numbering is uncertain due to some very small peaks of unknown origin. In the

[5] K. DRESSLER, Can. J. Phys. **47**, 547 [1969].

Table 2. States of $NO^+$, measured with 584 Å.

| State | $v$ | Energy (eV) midpoint | peak | Remarks |
|---|---|---|---|---|
| X $^1\Sigma^+$ | | | | Halfwidth 32 meV, no spin-orbit splitting |
| | 0 | 9.262 | | |
| | 1 | $9.553_2$ | | Calibrated |
| | 2 | 9.839 | | |
| | 3 | 10.121 | | |
| | 4 | $10.39_9$ | | |
| | 5 | $10.67_3$ | | Weak |
| a $^3\Sigma^+$ | | | | Halfwidth 29 meV, spin-orbit splitting 12 meV |
| | 0 | | 15.667 | |
| | 1 | 15.816 | 15.824 | |
| | 2 | 15.970 | 15.977 | |
| | 3 | $16.119_0$ | 16.126 | Calibrated |
| | 4 | 16.263 | 16.271 | |
| | 5 | 16.405 | 16.413 | |
| | 6 | | | |
| | 7 | 16.678 | 16.685 | |
| | 8 | 16.808 | 16.814 | |
| | 9 | | 16.942 | |
| | 10 | | $17.06_6$ | |
| b $^3\Pi$ | | | | Halfwidth 17 meV, no spin-orbit splitting |
| | 0 | 16.562 | 16.561 | |
| | 1 | $16.770_6$ | 16.771 | Calibrated |
| | 2 | | $16.97_1$ | Weak |
| w $^3\Delta$ | | | | Halfwidth 30 meV, spin-orbit splitting 12 meV |
| | 0 | 16.863 | 16.870 | |
| | 1 | 17.023 | 17.030 | |
| | 2 | $17.181_3$ | 17.189 | Calibrated |
| | 3 | 17.337 | 17.344 | |
| | 4 | 17.486 | 17.494 | |
| | 5 | 17.639 | 17.645 | |
| | 6 | 17.784 | 17.794 | |
| | 7 | 17.930 | 17.937 | |
| | 8 | 18.071 | 18.077 | |
| | 9 | $18.21_1$ | | Overlap |
| b′ $^3\Sigma^-$ | | | | Halfwidth 27 meV, spin-orbit splitting 12 meV |
| | 0 | $17.58_6$ | $17.59_2$ | |
| | 1 | 17.745 | 17.751 | |
| | 2 | 17.899 | 17.905 | |
| | 3 | 18.050 | 18.057 | |
| | 4 | $18.19_7$ | $18.20_3$ | |
| | 5 | | $18.35_0$ | |
| | 6 | $18.48_5$ | | |
| | 7 | $18.62_6$ | $18.63_5$ | |
| | 8 | $18.76_5$ | | Overlap |
| | 9 | $18.90_2$ | | Weak, overlap |
| A′ $^1\Sigma^-$ | | | | Halfwidth 29 meV, spin-orbit splitting 14 meV |
| | 0 | 17.811 | 17.818 | |
| | 1 | 17.966 | 17.972 | |
| | 2 | 18.119 | 18.124 | |

Table 2 continued.

| State | $v$ | Energy (eV) midpoint | peak | Remarks |
|---|---|---|---|---|
| | 3 | 18.268 | 18.274 | |
| | 4 | $18.414_4$ | 18.421 | Calibrated |
| | 5 | 18.554 | 18.561 | |
| | 6 | $18.69_3$ | | Overlap |
| | 7 | 18.830 | 18.837 | |
| | 8 | $18.96_3$ | 18.971 | |
| | 9 | $19.09_3$ | | |
| | 10 | 19.218 | | |
| | 11 | 19.34 | | Weak, overlap |
| A $^1\Pi$ | | | | Halfwidth 27 meV, spin-orbit splitting 13 meV |
| | 0 | 18.319 | 18.325 | |
| | 1 | 18.511 | 18.517 | |
| | 2 | 18.699 | 18.705 | |
| | 3 | 18.882 | | |
| W $^1\Delta$ | | | | Halfwidth 35 meV, spin-orbit splitting 16 meV |
| | 0 | | | Overlap |
| | 1 | | | Overlap |
| | 2 | 18.36 | | Overlap |
| | 3 | 18.50 | | Overlap |
| | 4 | $18.64_3$ | 18.650 | |
| | 5 | 18.780 | 18.788 | |
| | 6 | 18.914 | 18.923 | |
| | 7 | $19.04_4$ | $19.05_3$ | |
| | 8 | 19.172 | 19.181 | |
| | 9 | 19.298 | 19.307 | |
| | 10 | 19.412* | 19.426 | |
| | 11 | 19.528* | $19.53_9$ | |
| | 12 | 19.639* | | |
| | 13 | 19.746* | | |
| | 14 | 19.849* | | |
| | 15 | 19.948* | | |

* Measured with the 304 Å line.

ESCA measurements [6] this state is seen as a small peak at 23.3 eV, and there are no more peaks in the spectrum until at 40 eV where the $^3\Pi$ and $^1\Pi$ states from the $3\sigma$ electron appear.

O'Neil and Schaefer's calculations [4] on CO are in good agreement with our experimental results as to energies, nuclear distances and vibrational energies of $NO^+$ for all states below 20 eV and for B′ $^1\Sigma^+$. But for the higher $\Pi$-states the comparison is uncertain as the dissociation limits differ.

The peak at 21.7 eV has an irregular structure with very broad overlapping bands, Fig. 3. It seems to consist of two parts, one strong single peak at

[6] K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, D. F. Hedén, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, ESCA Applied to Free Molecules, North-Holland Publ. Co., Amsterdam 1969.

21.72 eV and a short band system of 5 or 6 peaks with about 50 meV vibrational energy.

We will interpret this band as consisting of c $^3\Pi$ and B $^1\Pi$, which we assume to be close to each other. We expect therefore this peak to be 4 times stronger than one $^1\Pi$ peak and 1.33 times stronger than one $^3\Pi$ peak. In our measurements (Table 3)

Table 3. Relative intensities of $NO^+$ states.

| State | Intensity |
|---|---|
| b $^3\Pi$ | 2.5 |
| A $^1\Pi$ | 1 |
| c $^3\Pi$ and B $^1\Pi$ | 2.5 |
| B′ $^1\Sigma^+$ | 0.8 |

the total intensity of the peak at 21.7 eV is approximately 2.5 times greater than that of the A $^1\Pi$ bands at 18.3 eV. In the ESCA measurements on NO by SIEGBAHN et al. [6] the peak at 21.7 eV is as much as 5 times stronger than the A $^1\Pi$ peak and about 2 times higher than the b $^3\Pi$ peak. The high ratios in the ESCA measurements may partly be due to the strong 2s-character of c $^3\Pi$ and B $^1\Pi$ (cf. calculations on NO by BRION, MOSER and YAMAZAKI [7]). The intensities therefore support our interpretation but are not conclusive.

## The 584 Å Spectrum of NO

At the best resolution the spin-orbit splitting can be observed. For most of the bands it is 12 – 16 meV but for the b $^3\Pi$ state and the X $^1\Sigma^+$ state it is absent.

Comparison with our earlier measurements shows good agreement within the error limits, except as to the a $^3\Sigma^+$ and the W $^1\Delta$ states, where the old energy values are as much as 10 meV too low. This was probably due to changed surface charges in the ionization chamber, which is always a problem in photoelectron measurements.

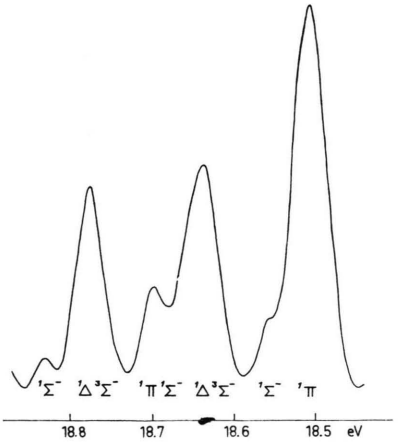


Fig. 5. Photoelectron spectrum of NO with 304 Å light. Resolution 25 meV.

The A′ $^1\Sigma^-$ state is weaker in the 304 Å spectrum than in the 584 Å spectrum compared with the adjacent $^1\Delta$ and $^3\Sigma^-$ bands, see Figs. 4 and 5. The higher vibrational levels of A $^1\Pi$ have comparably less intensity with the 304 Å line than with 584 Å light.

[7] H. BRION, C. MOSER, and M. YAMAZAKI, J. Chem. Phys. **30**, 673 [1959].