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AUTOIONIZATION STRUCTURE OF NITRIC OXIDE (NO) AT THE FIRST IONIZATION LIMIT

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Abstract

A new and more detailed interpretation is given to the fine structure in the photoionization curve of cold NO observed by Ng, Mahan and Lee ¹⁾. Resonances are assigned to autoionizing np and nd² Rydberg levels which give prominent diffuse absorption bands in a spectrum recorded with the synchrotron radiation continuum. $\Delta v < -1$ transitions in the vibrational autoionization process are substantiated.

I. Introduction

In 1976 Ng, Mahan and Lee ¹⁾ have published a photoionization curve of NO in the wavelength region 1340 - 1190 Å which comprises the first four well known vibrational steps $v = 0, 1, 2, 3$ of the ion NO^+ in its ground state. In addition to the step structure that indicates direct ionization, the curve shows the fine structure, first seen by Killgoar et al. ²⁾, much more pronounced since the measurements were made on NO molecules in a supersonically cooled molecular beam. The resonance structure is obtained with the spectral resolution of about 6 meV corresponding on the wavenumber scale to 50 cm^{-1} .

In the same year Miescher ³⁾ has published an atlas of the absorption spectrum of cold NO with the resolution of about 3 cm^{-1} in the region 1420 - 1250 Å, and a paper ⁴⁾ on a high resolution (0.1 cm^{-1}) study of the absorption structure in the same region. Prior knowledge ⁵⁾ on the nl-Rydberg series of NO was thus considerably extended by these publications.

The present paper proposes a modified and more detailed interpretation of the fine structure in the photoionization efficiency curve and a new analysis of the autoionization process. In addition it reports on some new results concerning the diffuse structure in the

absorption spectrum recorded with the synchrotron radiation continuum as the background.

II. The Rydberg series of NO

Ng et al. have assigned peaks in the photoionization curve to a single Rydberg series using a quantum defect $\delta = +0.87$. There is, however, no such series observed in absorption. The 4 series observed ⁶⁾, each with its vibrational structure, are ns with $\delta_s = +1.2$, np with $\delta_{p\sigma} = +0.68$, $\delta_{p\pi} = +0.74$, nd with $\delta_{d\sigma\pi} = -0.02$, $\delta_{d\delta} = +0.07$ and nf with a very small quantum defect. ns and nf of these series show sharp rotational levels, whereas np and nd δ show diffuseness at higher n. nd σ, π - X bands are very weak and are not observed in absorption for $n > 4$. Diffuseness of bands located below the ionization limit ($\lambda > 1340 \text{ Å}$) must be produced by predissociation. Above the limit autoionization is possible as a additional or alternative channel.

The photoionization efficiency curve of Ng et al. is reproduced again in Fig.1. The figure shows now the positions of the diffuse np and nd δ Rydberg levels for $v = 1, 2, 3, 4$ and 5. The majority of these levels is directly observed in the absorption spectrum. Their energies have been tabulated in ref. 3, 5 and 6. Others can safely be calculated. In some measure the degree of diffuseness of the absorption bands has been characterized in ref. 3. The shapes of the diffuse bands vary considerably and are often difficult to decipher from the high resolution pho-

tographic records because of overlapping lines of $nf-X$ bands. A photoelectrically scanned absorption spectrum of NO could recently be obtained with the smooth and steady continuum of the DORIS storage ring ⁷⁾ at Hamburg. In this experiment the absorption cell was again kept cold with liquid nitrogen and the resolution of the spectrometer, by using the 50 μm slit, was chosen low enough (8.5 cm^{-1}) to smooth away the overlapping sharp rotational lines. This procedure did bring into prominence the diffuse bands, though it does not give the true shapes. Fig.2 is the result, covering the wavenumber range of the first two vibrational steps in the ionization curve.

Only a few peaks of the low Rydberg members $n = 4, 5$ and 6 , corresponding to heads of the sharp $nf-X$ and $ns-X$ bands remain visible in the smeared-out spectrum, all the strong peaks are the diffuse $nd\delta-X$ and $np-X$ bands. The latter split into $p\pi$ and $p\sigma$, the two components rapidly narrowing with n . Peaks arising from the $3/2$ -component of the $^1\Pi$ ground state are small and are left unassigned. Based on the new spectrum some of the wavenumbers given in Table 1-3 are corrected compared to numbers given in ref. 3. Additional wavenumbers of diffuse bands are entered that had escaped detection by the photographic method.

III. Discussion

Fig. 1 immediately suggests an interpretation of the fine structure in the ionization curve different from the assignments made by Ng et al. The np and $nd\delta$ levels fit quite well the peaks when $\Delta v < -1$ transitions in the autoionization process are not a priori excluded as in ref. 1. The Tables 1 - 3 give the differences $i-a$ in cm^{-1} between the ionization peaks and the absorption data. They are well within the limits of the accuracy which, as mentioned above, is 50 cm^{-1} for well defined ionization peaks and to which the rotational spread of the absorption bands of about equal magnitude must be added. In cases where the latter are very diffuse or overlapping each other ($6p$ is overlapping $9p$) an additional uncertainty occurs. Many of the ionization peaks are correlated to several $nllv$ Rydberg levels in the tables. The letter s, m or w characterizes the quality of the ionization peak and Δv indicates the vibrational change for the autoionizing transition considered. The $|\Delta v|$ in Table 2 and 3 are minima. $\Delta v < -1$ transitions are numerous and several of them are unambiguous as particularly for $5p, 6p$ and $7p$ peaks. Other than in ref. 1 all peaks are taken as corresponding to molecules in the $X^1\Pi_{3/2}$ component of the ground state. There is now no need to have recourse on the $^2\Pi_{3/2}$ component and on non-equilibrium in the cold NO. ^{*)} More-

*) In fact, a recent investigation on free jet expansion of NO at room temperature by Reuss and coworkers concluded that the electronic relaxation of NO from $^2\Pi_{3/2}$ to $^2\Pi_{1/2}$ is as efficient as the translational relaxation during the expansion, and most of NO molecules in free jet beam were in $^2\Pi_{1/2}$ state ⁸⁾.

over, the evidence for assignments of the peaks to ground state doublets in ref.1 is not convincing, if one follows the individual pairs beyond $n = 9$, and if one has in view the intensity ratio of the spin-doublets.

The principal quantum number n of a level in a Rydberg series can be changed if the quantum defect δ is simultaneously changed by the same number of units. The quantum defect $\delta = 0.87$ used in ref.1 is close to 0.89 what is obtained as the mean of the quantum defects δ_p and $\delta_{d\delta} + 1$ with the values quoted in section II. Since the $nd\delta$ peaks in Fig.1 carry the number n smaller by one unit than the $3/2$ peaks in ref.1 and the np peaks the same n as the $1/2$ peaks in ref.1, it is not surprising that a representation of the series with $\delta = 0.87$ was possible.

The main result of the revised interpretation of the ionization curve is that $\Delta v = -1$ autoionizing transitions are not strongly favored, and that the autoionizing Rydberg levels are specified as np and nd levels. Only the small peak at 1263 \AA is left unassigned. Multiple assignments outweigh the single ones in Tables 1 to 3. A close inspection of the intensities intimates that ionization into multiple channels is real. For example, absorption to $5d\delta, v+1$ is seen in Fig.2 much stronger than the nearby absorption to $7d\delta, v$ and thus most likely it is the $5d\delta$ levels that are responsible for the height of the first peaks appearing at the steps in the ionization

curve in Fig.1. This peak is followed for $v = 1$ in Fig.1 by two barely separated smaller peaks and for $v = 2$ by a single high peak. $9p, v$ probably contributes little, but the strongly absorbing $6p\pi, v+1$ level can explain the difference in behavior because it coincides for $v = 2$ much closer with $8d\delta, v$ than for $v = 1$, see Table 1 and 2. Unobstructed $\Delta v = -2$ peaks are $7p, v$, clearly seen for $v = 2$ and weakly indicated for $v = 3$ and 4.

High absorption peaks occur in Fig.2 for the isolated $5p\pi$ levels. The peak is much broader for $v = 3$ than for $v = 4$ and furthermore $5p\sigma$ peaks are missing. Either observation is in accordance with previous reports ³⁾ where dissociative interaction with the $A'^2\Sigma^+$ continuum was considered as responsible for the anomalies. Fig.1 gives no evidence for autoionization of the $5p$ levels, clearest for the $5p\pi, 3$ level that is located right at a minimum in the ionization curve.

The theory of the autoionization process in molecules other than H_2 has been discussed comprehensively by Berry ⁹⁾ and detailed ab initio computations for the N_2 molecule have been published by Duzy and Berry ¹⁰⁾. No comparable study for the NO molecule is known. The conditions in NO are different owing to the lack of symmetry. As mentioned in section II the rotational structure of the higher np levels in NO is diffuse in opposition to the conditions for N_2 , and diffuseness in absorption can for NO always

result from predissociation because of the low dissociation energy. It has been previously emphasized ¹¹⁾ that the excited states of $^2\Delta$ symmetry are less exposed to predissociation than the $^2\Pi$ states. In emission spectra up to 70500 cm^{-1} only the $^2\Delta - X$ bands are observed above the dissociation energy. None of the bands in the much higher energy range of Fig.2 has been observed in emission, but it is reasonable to assume that the stability of the higher $nd\delta$ states in that region is still preserved and thus can give autoionization a good chance.

That ns and nf rotational levels appear in absorption sharp within the instrumental width of 0.1 cm^{-1} does not exclude by itself the possibility of autoionization of these levels. nf peaks would not be separated from the $nd\delta$ peaks in Fig.1. These levels are excluded because of their weak interaction with the core. The ns levels are excluded because of absence of peaks in Fig.1 at energies where for $n < 9$ they would be sufficiently isolated if they existed.

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Table I. Autoionization peaks (i) in the Rydberg series converging to the limit $v=1$ of $X^1\Sigma^+$ of NO^+ . Possible assignments to absorption levels (a) carrying the quantum numbers $n\lambda v$. Δv = vibrational change in autoionizing transition.

| | i | a | i-a | $n\lambda v$ | Δv |
|-----------|------------------|------------------------------------|------------------------------|---|----------------------|
| λ | cm^{-1} | | | | |
| 1336.67 s | 74813 | 74780 74860 | + 13 - 47 | 7d δ 1 5d δ 2 | -1 -2 |
| 1334.17 s | 74953 | 74995* | - 42 | 8p 1 | -1 |
| 1327.67 m | 75320 | 75315 75400 | + 5 - 80 | 8d δ 1 6p π 2 | -1 -2 |
| 1324.17 m | 75519 | 75475 75500 75620 | + 44 + 19 -101 | 9p 1 6p σ 2 5p π 3 | -1 -2 -3 |
| 1321.17 m | 75690 | 75690 75690* 75760* 75800 | 0 0 - 70 -110 | 9d δ 1 4p π 5 5p σ 3 10p 1 | -1 -5 -3 -1 |
| 1316.67 m | 75949 | 75800 75890 75960 76024 | +149 + 59 - 11 - 75 | 10p 1 4p σ 5 10d δ 1 11p 1 | -1 -5 -1 -1 |
| 1313.17 w | 76152 | 76150* 76200 76240 | + 2 - 48 - 88 | 11d δ 1 12p 1 6d δ 2 | -1 -1 -2 |
| 1310.0 m | 76336 | 76300* | + 36 | 12d δ 1 | -1 |
| 1305.3 m | 76611 | 76590 76650 | + 21 - 39 | 7p π 2 7p σ 2 | -2 -2 |
| 1300.5 w | 76894 | 76830 | + 64 | 4d δ 4 | -4 |

* calculated.

s, m, w = strong, medium, weak, respectively.

Table II. Same as Table I, but series converging to the limit $v=2$.

| | i | a | i-a | $n\lambda v$ | Δv |
|-----------|------------------|---------------------------|----------------------|--|----------------|
| λ | cm^{-1} | | | | |
| 1296.17 s | 77150 | 77085 77150 | + 65 0 | 7d δ 2 5d δ 3 | -1 -2 |
| 1293.67 w | 77299 | 77290 | + 9 | 8p 2 | -1 |
| 1287.67 s | 77660 | 77630 77670 | + 30 - 10 | 8d δ 2 6p π 3 | -1 -2 |
| 1285.17 w | 77811 | 77750 77760 77850 | + 61 + 51 - 39 | 9p 2 6p σ 3 5p π 4 | -1 -2 -3 |
| 1281.67 m | 78023 | 78000* 78000 78090 | + 23 + 23 - 67 | 5p σ 4 9d δ 2 10p 2 | -3 -1 -1 |
| 1277.67 m | 78267 | 78270* 78330* | - 3 - 63 | 10d δ 2 11p 2 | -1 -1 |
| 1275.17 m | 78421 | 78330* 78460* 78530 | + 91 - 39 -109 | 11p 2 11d δ 2 6d δ 3 | -1 -1 -2 |
| 1268.1 w | 78858 | 78850 78920* | + 8 - 62 | 7p π 3 7p σ 3 | -2 -2 |
| 1265.5 w | 79020 | 79030* | - 10 | 4d δ 5 | -4 |
| 1263.0 w | 79177 | | | ? | |

Table III. Same as Table I, but series converging to the limit $v=3$.

| λ | i | a | i-a | nl λ | v | Δv |
|------------------------|-------|--------------------------------------|----------------------------|--|------------------|----------------------|
| | | cm ⁻¹ | | | | |
| 1259.17 m | 79417 | 79375* 79385 | + 42 + 32 | 7d δ 5d δ | 3 4 | -1 -2 |
| 1256.67 m | 79575 | 79580 | - 5 | 8p | 3 | -1 |
| 1250.67 m | 79957 | 79910* 79930* 80027* | + 47 + 27 - 70 | 8d δ 6p π 6p σ | 3 4 4 | -1 -2 -2 |
| 1249.17 s | 80053 | 80027* 80045* 80050* 80225* | + 26 + 8 + 3 -172 | 6p σ 5p π 9p 5p σ | 4 5 3 5 | -2 -3 -1 -3 |
| 1245.17 w | 80310 | 80225* 80280* | + 85 + 30 | 5p σ 9d δ | 5 3 | -3 -1 |
| 1243.67 w | 80407 | 80280* 80395* | +127 + 12 | 9d δ 10p | 3 3 | -1 -1 |
| 1241.67 w | 80537 | 80543* | - 6 | 10d δ | 3 | -1 |
| 1240.17 w | 80634 | 80630* | + 4 | 11p | 3 | -1 |
| 1238.67 [†] w | 80732 | 80735* 80780* | - 3 - 48 | 11d δ 6d δ | 3 4 | -1 -2 |
| 1236.67 w | 80862 | 80780* | + 82 | 6d δ | 4 | -2 |
| 1233.8 w | 81050 | 81100* | - 50 | 7p π | 4 | -2 |
| 1232.3 w | 81149 | 81170* | - 21 | 7p σ | 4 | -2 |

[†] error in ref.1 corrected.

Figure Captions

Fig.1 The photoionization efficiency curve of NO (Ng, Mahan and Lee¹). nd = δ -component of the d complex.

Fig.2 Absorption spectrum of cold H₂O, obtained with the synchrotron continuum of the DORIS storage ring (DESY, Hamburg) with the resolution of 8.5 cm⁻¹. Length of the absorption cell 52 cm, pressure 0.2 torr. nd = δ -component of the d complex.

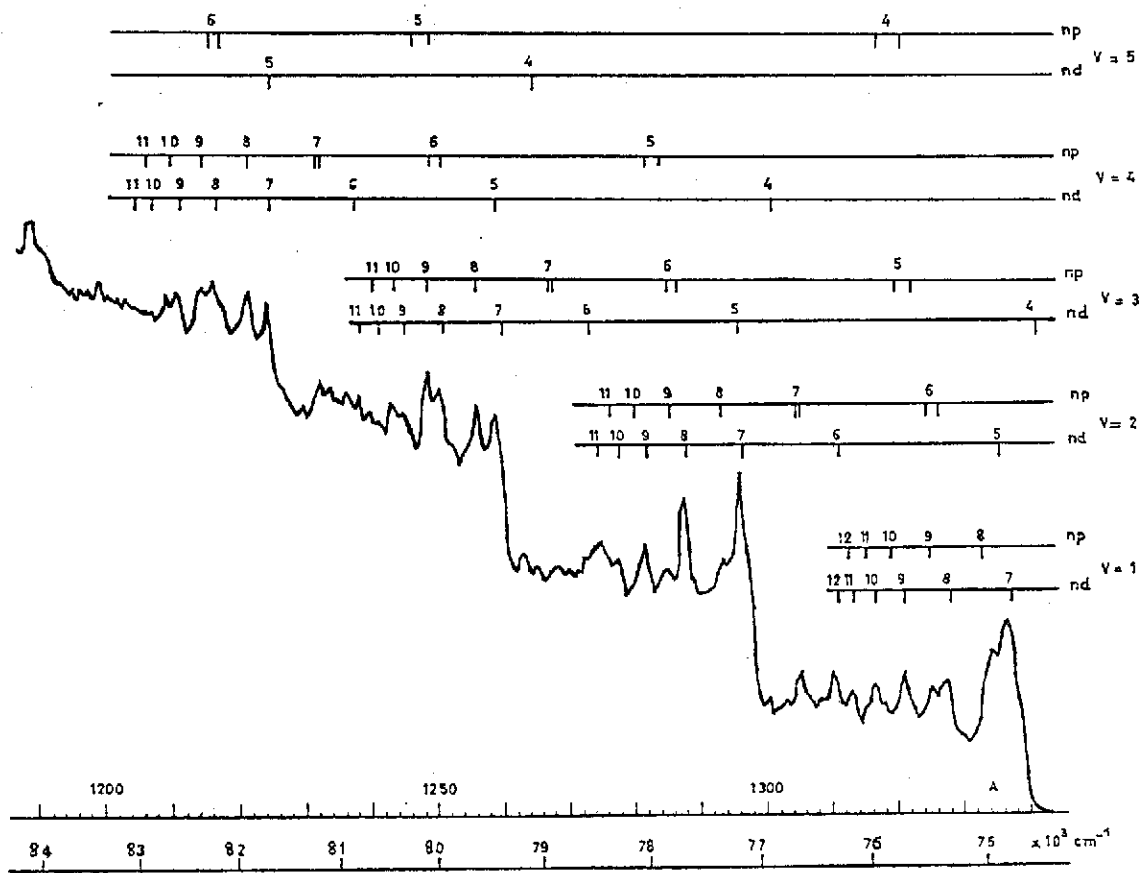


Fig. 1

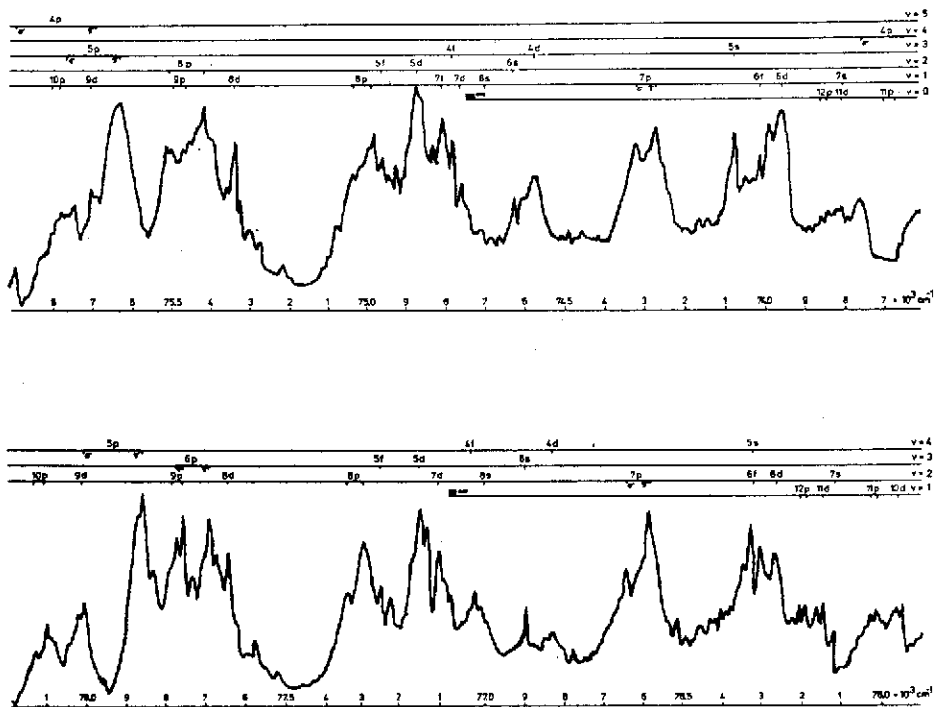


Fig. 2