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Absorption Structure Near the *K* Edge of the Nitrogen Molecule*

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The absorption spectrum of the nitrogen molecule in the 30 Å region has been studied photographically, using synchrotron radiation from a 1.3-BeV electron synchrotron as the background continuum. A 2-m grazing incidence spectrograph with a glass grating was used to take the absorption spectrum. Discrete structure has been observed near the *K* edge of nitrogen. On the basis of electron configuration, the absorption data obtained are compared with the optical spectroscopic data of the NO molecule and it is found that the absorption structure is well explained as due to the excitations of a 1*s* electron to outer-shell orbitals of the nitrogen molecule. The energy value of 409.5 ± 0.1 eV is obtained for the *K* level of the nitrogen molecule.

As mentioned in a previous letter on argon *L* absorption,[1] absorption measurements of gases in the extreme uv and soft x-ray regions have been undertaken for the past few years by the Institute for Nuclear Study–Synchrotron Orbital Radiation (INS-SOR) group with a 1.3-BeV electron synchrotron at the Institute for Nuclear Study, the University of Tokyo, as a continuum light source.

In the extreme uv region, especially from 600 Å down to 80 Å, absorption measurements of gases have been carried out extensively by Madden and Codling[2] by using the electron synchrotron at the National Bureau of Standards(NBS). On the other hand, in the region around 10 to 100 Å, there have been only a few measurements of the absorptions of gases. This can probably be attributed to the difficulty in obtaining a suitable continuum light source in this particular region.

The present paper shows the preliminary result obtained for the absorption structure near the *K* edge of the nitrogen molecule in the 30 Å region by means of the continuum light emitted from the electron synchrotron at the Institute for Nuclear Study, and also by means of photographic detection with a vacuum spectrograph.

The spectrograph used is a 2-m grazing incidence vacuum type which utilizes a 1080-lines/mm glass grating at an angle of incidence of 87°. It is connected to the synchrotron doughnut through a duct that is 8-m long. The resolution obtained is somewhat better than 0.03 Å with a slit width of about 10 μ in the 120 Å region, where the fourth-order spectrum of the *K* absorption of nitrogen lies; most absorption measurements for nitrogen were made with the fourth-order spectra.

The electron synchrotron was operated mostly in the energy range between 850 MeV and 1.2 BeV, for which the intensity peak lies in a wavelength range of about 5 to 20 Å. In the absorption experiment, prepurified tank nitrogen gas was introduced into the main chamber of the spectrograph. Nitrogen gas which had leaked into the duct through the entrance slit was evacuated with a differential pumping system in order to maintain the synchrotron doughnut pressure below 5×10^{-6} Torr. For the gas pressure higher than 1 Torr in the spectrograph the capacity of the differential pumping system was insufficient to insure high vacuum inside the duct. Therefore, when gas pressure higher than 1 Torr was required, a thin film of nitrocellulose held on a nickel mesh was placed as a window in front of the entrance slit to separate the spectrograph from the high-vacuum side.

The absorption spectra were photographed with Kodak SWR plates. Emission lines produced by a sliding spark were used as comparison lines for the determination of the wavelengths of the absorption spectra. The sliding spark discharge tube is attached to the entrance slit unit of the spectrograph with a special device which enables the discharge tube to move onto and away from the optical axis of the entrance slit by simple rotation without breaking the vacuum.

Figure 1 shows a spectrum of nitrogen *K* absorption near 30 Å. This spectrum was taken in the

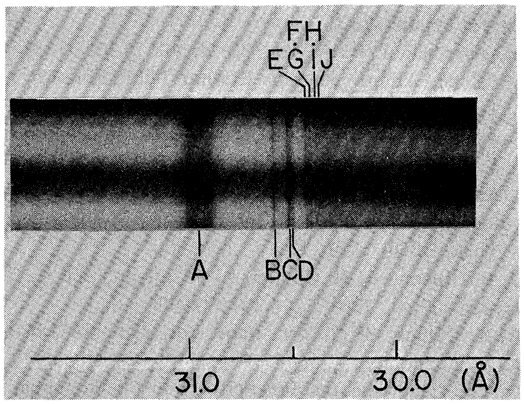

FIG. 1. Absorption spectrum of N_2 molecule in the 30 Å region. This spectrum was taken under the following conditions. Energy of synchrotron: 930 MeV, pressure of gas: N_2 (1.5 Torr) + O_2 (4 Torr), exposure time: 30 min.

fourth order at a nitrogen pressure of 1.5 Torr, with a path length of about 45 cm and an exposure time of 30 min. In most cases, including the case for Fig. 1, oxygen gas having a pressure of 2 to 4 Torr was introduced into the spectrograph besides the nitrogen; this was done in order to eliminate undesirable order overlapping due to the intense light having wavelengths shorter than 20 Å, since the oxygen shows strong absorption below 20 Å. It was almost impossible to obtain the details of the absorption structure without this provision, because higher-order spectra of shorter wavelengths overlapped the spectrum concerned and smeared out the details of the absorption structure. In Fig. 2 is shown a densitometer trace of the spectrum in Fig. 1. The absorption structure seen in Figs. 1 and 2 is apparently due to transitions, caused by 1s electron excitation, from the ground state of nitrogen to highly lying molecular states followed by a photo-ionization continuum level.

The ground state of the nitrogen molecule has the electron configuration

$$(\sigma_g 1s)^2(\sigma_u 1s)^2(\sigma_g 2s)^2(\sigma_u 2s)^2\ (\pi_u 2p)^4(\sigma_g 2p)^2,\ {}^1\Sigma_g^+ .$$

When one of the electrons in the K orbital is excited to an outer-shell orbital by absorbing a photon, the electron configulation for the outer-shell orbitals of such a highly excited N_2 molecule is nearly the same as that of the NO molecule except for the difference in the electron configurations for nonbonding K orbitals of the both molecules. It is, therefore, expected that the highly lying states of the N_2 molecule should have almost the same relative energy levels as those of the NO molecule. On this assumption, the absorption bands obtained in the present experiment have been compared with the optical spectroscopic data of the NO molecule[3] and tentatively assigned as follows.

The strong and broad band at the longest wavelength (A in the figures) is obviously due to an excitation from the ground state to the upper state which has the configuration of $(\sigma_u 1s)^{-1}(\pi_g 2p)$, ${}^1\Pi_u$. By $(\sigma_u 1s)^{-1}$ we mean an excitation of one of the electrons in the $(\sigma_u 1s)$ orbital. If we ignore the binding energy of the $(\sigma_u 1s)$ electron, it can be said that this excited state corresponds to the ground state of the NO molecule.

The next sharp absorption band (B) at 4.75 eV above the center of the first strong absorption band can be attributed to an excitation to the first member of the Rydberg states with the configurations $(\sigma_u 1s)^{-1} ns\sigma_g$, ${}^1\Sigma_u^+$, $(n \geqslant 3)$. The first member with the configuration $(\sigma_u 1s)^{-1} 3s\sigma_g$, ${}^1\Sigma_u^+$ is considered as the one corresponding to the $A^2\Sigma^+$ state of the NO molecule which is the lowest of the Rydberg states.

The third absorption band (C and D) at about 6 eV above the first band is rather broad and slightly resolved into two sub-bands which are probably due to excitations to the first members of two different Rydberg states whose configurations are $(\sigma_g 1s)^{-1} 3p\pi_u$, ${}^1\Pi_u$ and $(\sigma_g 1s)^{-1} 3p\sigma_u$, ${}^1\Sigma_u^+$; these states correspond to the $C^2\Pi$ and $D^2\Sigma^+$ states of the NO molecule.

The fourth absorption band (E, F, and G)consists of at least two sub-bands. There might be three bands instead of two, because at this energy the analogy with the NO molecule suggests the possibility of transitions to Rydberg states with the configurations $(\sigma_u 1s)^{-1} 4s\sigma_g$, ${}^1\Sigma_u^+$, $(\sigma_u 1s)^{-1} 3d\pi_g$, ${}^1\Pi_u$, and $(\sigma_u 1s)^{-1} 3d\sigma_g$, ${}^1\Sigma_u^+$, which correspond to the $E^2\Sigma^+$, $H'^2\Pi$, and $H^2\Sigma^+$ states of the NO molecule.

Finally there is another absorption band (H and I) near the edge of the continuum absorption. This band may be related to either or both of the states $(\sigma_g 1s)^{-1} 4p\pi_u$, ${}^1\Pi_u$ and $(\sigma_g 1s)^{-1} 4p\sigma_u$, ${}^1\Sigma_u^+$, which correspond to the $K^2\Pi$ and $M^2\Sigma^+$ states of the NO molecule.

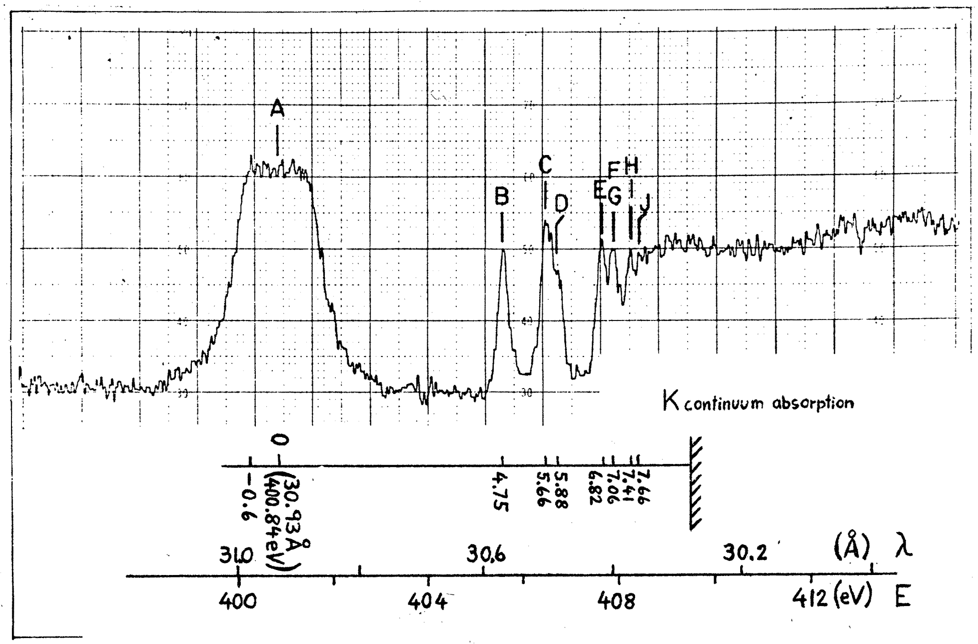

Fig. 2. Densitometer trace of $N_2 K$ absorption spectrum. This trace is of the spectrum shown in Fig. 1.

Energy differences of all these absorption bands from the first strong-absorption band agree well with those of the Rydberg states of the NO molecule from its ground state, if we shift the zero point for measuring the energy difference of each band by 0.60 eV from the center of the first absorption band toward the lower energies; this is because the absorption to the $v=0$ level of the $(\sigma_u 1s)^{-1}(\pi_g 2p)$, $^1\Pi_u$ state must appear near the threshold of the absorption band instead of its center.

With the above assignment, the present experimental absorption data are compatible with the theoretical expectations for the excited states originating from the $1s$ electron excitations.

The energy value of 409.5 ± 0.1 eV is obtained for the K energy level of the nitrogen molecule, using the ionization energy of the NO molecule (9.27 eV) and the energy values where the absorption bands appear in the present experiment.

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Series Perturbations and Atomic Oscillator Strengths: The ^2D Series of Al I*

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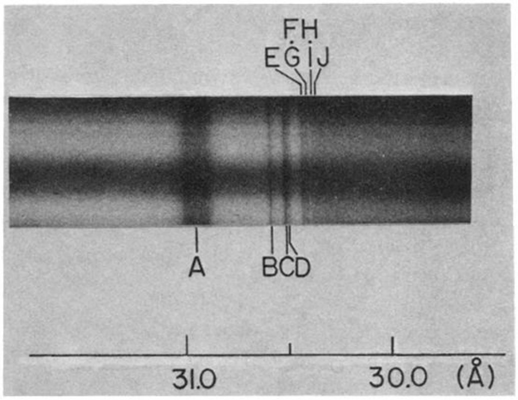
A model calculation has been made of the effects of perturbations of the $3s^2nd$ series of aluminum by the $3s3p^2\,{}^2D$ term. The model employed is the traditional one of configuration interaction among the independent-particle model representations of the relevant discrete states, with Hartree-Fock functions being used to compute the necessary matrix elements. It is found that, while in the Hartree-Fock approximation the $3s3p^2$ term is bound and embedded in the $3s^2nd$ series, the configuration interaction gives rise to a new autoionizing state just beyond the series limit. This state, which is approximately 50% $3s3p^2$, is found to have most of the ^2D absorption oscillator strength ($f=1.1$). The general properties of this model of series perturbations are also discussed in some detail.

INTRODUCTION

This paper reports the results of a configuration-interaction study of the term scheme and oscillator-strength distribution in an atomic Rydberg series perturbed by a single foreign term. Such perturbations have long been familiar in atomic spectroscopy where they produce an otherwise anomalous behavior in the quantum defects and term splittings along the series. These effects are normally so striking as to clearly identify the perturbing state.[1,2]

A particularly interesting example of a perturbed series appears in the spectrum of neutral aluminum, where the $3s^2nd\,{}^2D$ series should be strongly perturbed by the ^2D term of $3s3p^2$. The feature of interest in this case is the fact that the perturber can't seem to be found. Both Hartree-Fock calculations and semi-empirical estimates of the Slater parameters place the $3s3p^2$ term in the middle of the series – between $5d$ and $6d$. However, the latest experimental data[3] (quantum defects and doublet splittings) does not provide any unambiguous identification of the perturber, suggesting that the configuration interaction is quite strong with its effects spread out



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