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Observation of Vibrational Fine Structure in X-Ray Emission Lines

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We have recorded the x-ray emission spectrum of N_2, and resolved and identified the lines corresponding to the three outermost valence orbitals. We have observed vibrational fine structure within these x-ray emission lines.

Crystal spectrometers for x rays are capable of a very high resolution. However, since the distances between the reflecting layers in most crystals are in the range 1–10 Å, the studies are limited to x rays of fairly short wavelengths. The line shape of such radiation is therefore often obscured by the inherent width of the inner atomic orbital involved in the transition. With a grating spectrometer at grazing incidence, the wavelength region can be extended to comprise also the ultrasoft x rays (> 20 Å), which are produced in lighter atoms or in transitions between narrow outer orbitals in heavier atoms. The width of the *K* level in, e.g., carbon, nitrogen, or oxygen is presumably around 0.1 eV, and in x-ray spectra from such elements it would be possible to resolve the valence level structure in free molecules. For this purpose a high-resolution grating spectrograph designed for soft x rays from gaseous compounds was recently built in our laboratory. A brief description of the instrument and some preliminary results have been published elsewhere.[1-3] The grating has a concave radius of 3 m and is ruled with 540 lines/mm. The spectrograph is capable of a resolving power of ~3000. The x-ray spectra from gaseous samples are excited with direct electron bombardment. The electron beam from a 10-kV and 100-mA electron gun is directed into a collision chamber where a gas pressure of $\lesssim 1$ Torr is maintained.

The nitrogen molecule, being a simple homonuclear diatomic molecule, has been chosen for the present investigation. The electron spectrum of N_2 is well known,[4,5] but to our knowledge there is only one x-ray emission study reported.[6] However, the resolution in that case was too low to resolve the valence orbitals. In the present

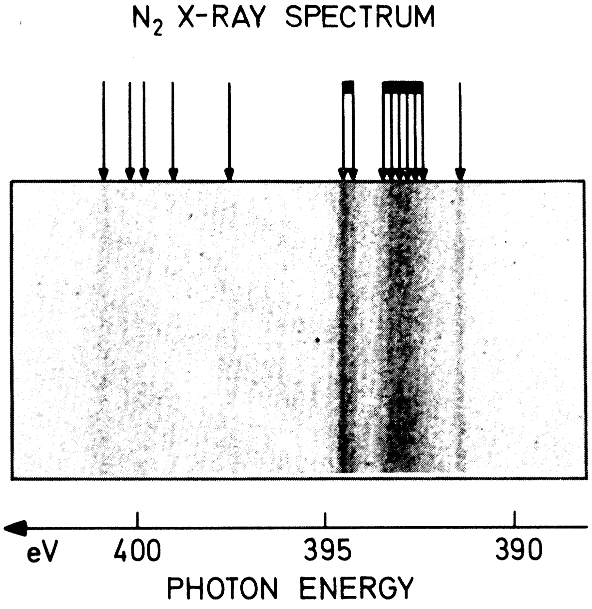

FIG. 1. X-ray emission spectrum of N_2 (third order).

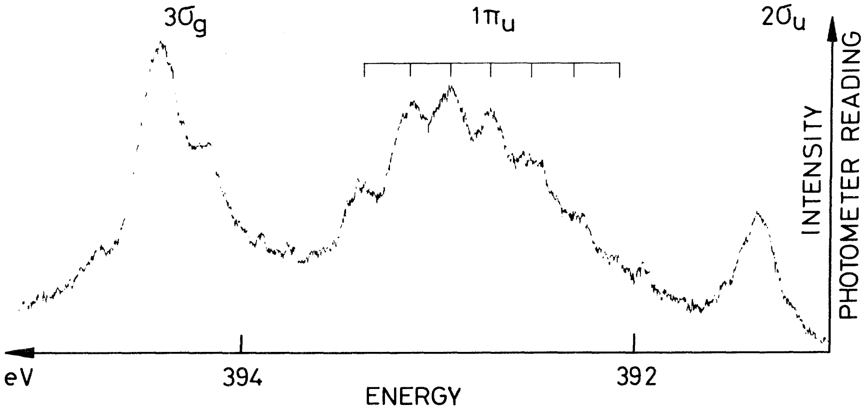

FIG. 2. Densitometer curve of the three main lines in Fig. 1.

experiment the emission spectrum from N_2 was recorded in first, second, third, and higher orders. The photographic recording of the third-order spectrum is shown in Fig. 1. As a guide for the eye the different emission lines which can be observed in this spectrum have been indicated. As can be seen, some of the lines are broadened, and one line in particular has been broadened to what appears as a band. At closer inspection one finds that this band in fact consists of a number of closely spaced lines as is shown in the densitometer curve in Fig. 2.

Our interpretation of the spectrum is the following: The electron configuration of N_2 in the ground state is $1\sigma_g^2 1\sigma_u^2$ ($N1s$) $2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2$; $^1\Sigma_g^+$. A direct comparison between results from electron spectroscopy for chemical analysis and our present ones leads to an immediate identification of the $N1s \leftarrow 3\sigma_g$, $N1s \leftarrow 1\pi_u$, and $N1s \leftarrow 2\sigma_u$ lines as shown in Fig. 2. The first two of these lines exhibit fine structure. The $3\sigma_g$ line has a weaker component at 0.23 eV lower energy. The $1\pi_u$ line is rather a progression of lines with an average spacing of 0.20 eV. The equal spacing between the lines and the magnitude of this spacing is indicative of molecular vibration. We therefore conclude that the observed fine structure is in fact a vibrational splitting. To our knowledge this fine structure within x-ray emission lines has not been observed before. A more complete interpretation of the high-resolution x-ray spectrum of molecular nitrogen and other molecules will be reported elsewhere.

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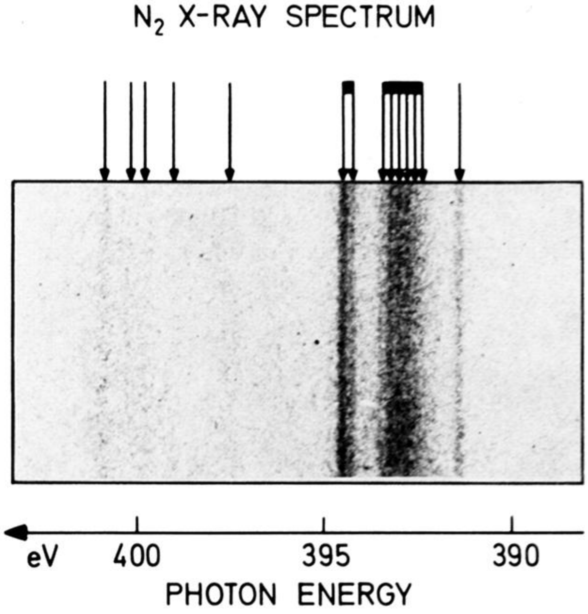

FIG. 1. X-ray emission spectrum of N_2 (third order).