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Rotational line profiles in the He I–excited photoelectron spectrum of the N_2 molecule

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The rotational line profiles of the $v=0$ peaks of the outer-valence X and B states in the photoelectron spectrum of N_2 have been observed. The line associated with transitions to the $X\,^2\Sigma_g^+(v=0)$ state shows a central peak reflecting the $\Delta N=0$ transitions surrounded by pronounced features corresponding to $\Delta N=\pm 2$ and ± 4 transitions. The $B\,^2\Sigma_u^+(v=0)$ state shows a doublet structure associated with $\Delta N=\pm 1$ transitions and weaker structures corresponding to transitions with $\Delta N=\pm 3$. The assignments are supported and quantified by simulations of the line profiles.

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The outer-valence UV photoelectron spectrum of the N_2 molecule is well known at least as regards the main features corresponding to transitions to the $X\,^2\Sigma_g^+$, $A\,^2\Pi_u$, and $B\,^2\Sigma_u^+$ cationic states. The inner valence region has also been studied with ultraviolet photoemission spectroscopy (UPS) and vibrational structure has been observed in the $C\,^2\Sigma_u^+$ and $3\,^2\Sigma_g^+$ states [1–3].

In UPS it is usually very difficult to obtain a spectrometer width that is better than about 10 meV. At this level of resolution the rotational line profiles can be studied only in special cases where the rotational energy spacings are large. The best examples are the H_2 and D_2 molecules, for which the individual rotational transitions can actually be resolved [4–7]. However, rotational structure has also been studied in several other cases [8–15].

In the case of the N_2 molecule, Allen and Grimm [16] used a deconvolution procedure to derive the rotational profiles of the lines of their He I photoelectron spectrum, which was recorded at a resolution of about 10 meV. We have now recorded the same $v=0$ components as in Ref. [16] at a resolution level of 4.5 meV.

The photoelectron spectrometer, which is of the hemispherical type, has been described in some detail elsewhere [17]. The gas cell has been supplied with electrodes in order to compensate for a field gradient which tends to lower the resolution [18]. Also, the background intensity has been reduced considerably. Therefore most of the intensity in the present spectra is significant, which is important in order to identify rotational transitions involving large changes in the rotational quantum number. The ionizing radiation is produced by a microwave powered electron-cyclotron-resonance source designed in this laboratory [19]. This source is extremely brilliant and has a measured linewidth of 1.2 meV.

In order to check the stability and the spectrometer function the line profiles were recorded using a 50% N_2, 50% Ne mixture in the gas cell. The Ne$2p_{3/2}$ line with a binding energy of 21.565 eV was recorded using the He I β component at 23.087 eV for the ionization, immediately before and after the recordings of the N_2 lines. The total recording time was 5 minutes and the energy step was 1.0 meV. The full width at half maximum of the Ne line was found to be 5.7 meV. Since the Doppler broadening is 3.4 meV for this line, the spectrometer resolution was 4.5 meV assuming Gaussian distributions. The energy scale was calibrated against the Ne line, and should be accurate to within ±1 meV for the $B\,^2\Sigma_u^+$ line and ±2 meV for the $X\,^2\Sigma_g^+$ line.

Figure 1 shows the lines recorded. For nitrogen they correspond to transitions from the vibrationless neutral ground state to the $v=0$ level of the $X\,^2\Sigma_g^+$ and $B\,^2\Sigma_u^+$ states of $N_2{}^+$. The observed line shapes correspond qualitatively very well to the rotational profiles expected from theoretical arguments. Rotational selection rules (e.g., [20,21]) suggest that transitions to the $X\,^2\Sigma_g^+$ cationic state may occur with a change $\Delta N=0$, ± 2, ± 4, etc. in the rotational angular momentum. The maximum intensity is expected for the $\Delta N=0$ transition, while the transitions involving a change in the rotational quantum number should decrease gradually as observed.

For transitions to the $B\,^2\Sigma_u^+$ cationic state it would be expected that only such transitions take place that involve a change in the rotational angular momentum by an odd quantum number, i.e., $\Delta N=\pm 1$, ± 3, etc. where the $\Delta N=\pm 1$ components are expected to dominate the spectrum. As can be seen from Fig. 1 this agrees well with the observations.

In order to verify these assignments and to obtain quantitative values on the probabilities for transitions involving different ΔN, we have simulated the observed spectra using the energy levels of the simple rotator [22]. The relative intensity for the individual rotational transition was simply obtained using the relative number of molecules N_J in the rotational level J of the lowest vibrational state at the temperature T given by the formula [22]

$$N_J \sim (2J+1)\exp\left[-\frac{hcB}{kT}J(J+1)\right],$$

where

$$B=\frac{h}{8\pi^2 cI}.$$

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B is the rotational constant and I is the moment of inertia. However, since N_2 is a homonuclear molecule, and the nitrogen nucleus has a spin which is equal to 1, the rotational energy levels characterized by even- and odd-J quantum numbers will have different statistical weights. Also taking this into account, the relative intensities of the different transitions are given by

$$I=6N_J k_{\Delta N} \quad \text{for even values of } J$$

and

$$I=3N_J k_{\Delta N} \quad \text{for odd values of } J\ .$$

Here $k_{\Delta N}$ is a factor containing, e.g., the overlap integral between the states. The factor has been used as a fitting parameter in the calculations. The calculations for the $X\,^1\Sigma_g^+(N_2)\rightarrow X\,^2\Sigma_g^+(N_2{}^+)$ transitions were carried out for rotational quantum numbers N corresponding to $\Delta N=0$, ± 2, and ± 4 and the 25 lowest rotational transitions were included for each ΔN. The energy levels were calculated using the equilibrium bond distances given in Ref. [23]. The expected width of the individual components is 7.2 meV assuming a spectrometer broadening of 4.5 meV and a Doppler broadening of 5.6 meV. However, the best fit to the experimental spectrum was obtained for a slightly higher value, 7.9 meV.

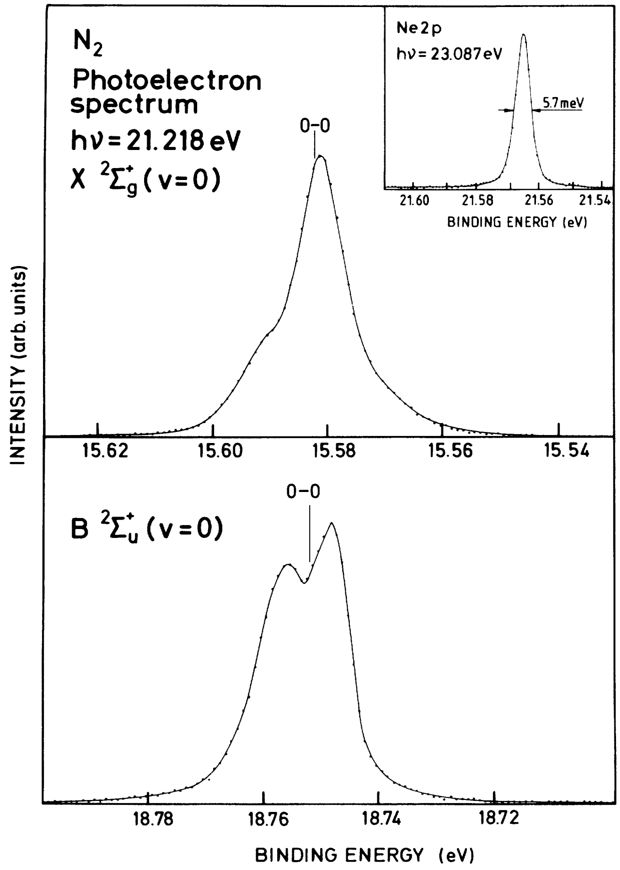

FIG. 1. The upper part shows the He I excited photoelectron spectrum corresponding to the $X\,^1\Sigma_g^+(N_2,\ v=0)\rightarrow X\,^2\Sigma_g^+(N_2{}^+,\ v=0)$ transition. The lower part shows the He I excited photoelectron spectrum corresponding to the $X\,^1\Sigma_g^+(N_2,(N_2,\ v=0)\rightarrow B\,^2\Sigma_u^+(N_2{}^+,\ v=0)$ transition. In the upper right part the Ne $2p_{3/2}$ line excited with the He I β radiation at 23.087 eV is inserted. The lines connecting the experimental points are drawn as guides to the eye.

Figure 2 shows the result obtained and includes, in addition to the experimental and calculated spectra, also the various subbands corresponding to different values of ΔN. From this fitting, the transition between the zero rotational levels (0-0) is found to be located at 15.581 (eV), in close agreement with the energy given in Ref. [23]. The $\Delta N=0$ transitions take about 47% of the total intensity, while the $\Delta N=\pm 2$ and ± 4 transitions take about 24% and 2%, respectively. The part of the total intensity which is associated with $\Delta N=0$ transitions is thus much smaller than what was found in Ref. [16], where a deconvolution procedure was employed in order to resolve the various ΔN subbands. In that study the spectrum was found to consist essentially of a single spike corresponding to the $\Delta N=0$ transitions.

The widths obtained for the $\Delta N=0$, $+2$, and -2 transitions in Fig. 2 are 8.3, 11.9, and 13.9 meV, respectively. The larger width of the components with negative ΔN compared to those with positive ΔN gives rise to the asymmetry of the lines and reflects the fact that the bond distance of the ionic state is larger than that of the neutral ground state.

The calculations for the $X\,^1\Sigma_g^+(N_2)\rightarrow B\,^2\Sigma_u^+(N_2{}^+)$ transitions were carried out for transitions corresponding to $\Delta N=\pm 1$ and ± 3, again including the 25 lowest rotational transitions. The energy levels of a static rotator were used along with intensities given by the statistical weights W as above. The expected photoelectron linewidth is 5.8 meV, assuming a spectrometer broadening of 4.5 meV and a Doppler broadening of 3.7 meV. As in the case of the $X\,^2\Sigma_g{}^+$ state, the best fit to the experimental spectrum was obtained for a slightly higher value,

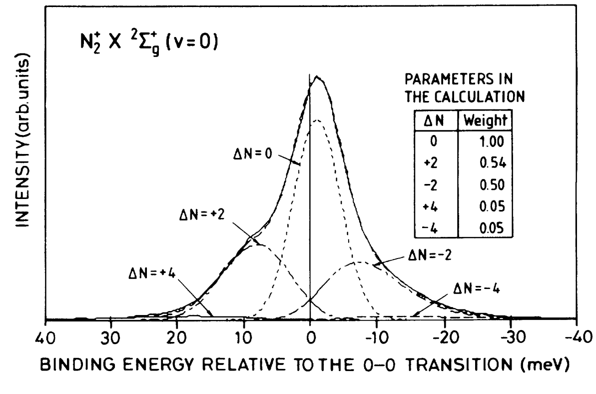

FIG. 2. The experimental (full line) and fitted theoretical (dashed line) $X\,^1\Sigma_g^+(N_2,\ v=0)\rightarrow X\,^2\Sigma_g^+(N_2{}^+,\ v=0)$ spectra shown together. The spectra are very similar and differences can be seen only on close inspection. For clarity the subbands corresponding to transitions with $\Delta N=0$, ± 2, and ± 4 are included. Also the weights used in the fitting of the theoretical spectrum are shown in the figure normalized to 1.00 for the $\Delta N=0$ subband. The energy scale refers to zero at the 0-0 transition.

6.3 meV.

Figure 3 shows the result obtained for the $X\,^1\Sigma_g^+(\mathrm{N}_2)\rightarrow B\,^2\Sigma_u^+(\mathrm{N}_2{}^+)$ transitions. From this fitting, the energy difference between the zero rotational levels (0-0) is found to be 18.751 eV, in close agreement with Ref. [23]. The $\Delta N=\pm1$ transitions take about 46% and 38%, respectively, of the intensity whereas the $\Delta N=\pm3$ transitions take about 8% each. It may be noted that the intensity of the $\Delta N=+1$ subband is approximately 20% higher than the $\Delta N=-1$ intensity which suggests that the overlap integral between rotational states connected by $\Delta N=+1$ is larger than for the counterparts with $\Delta N=-1$. We have therefore carried out separate intensity calculations based on the formulas for line strengths derived by Hönl and London [24] (cf. also Ref. [22], p. 208). In this case the weight factor for $\Delta N=+1$ is $J+1$, whereas for $\Delta N=-1$ it is equal to J. This fit gives a ratio between the factors $k_{\Delta N}$ for the $\Delta N=+1$ and $\Delta N=-1$ transitions which is approximately inverted to the results obtained when only the initial degeneracy is taken into account. Thus neither of these models is sufficient to explain the observed intensity relations in detail.

The widths for the $\Delta N=+1$ and -1 subbands are 8.0 and 7.3 meV, respectively. This difference is even more pronounced for the $\Delta N=+3$ and -3 subbands, which have widths of 22 and 17 meV, respectively. This explains the tail observed on the high binding energy side of the photoelectron band and shows that the bond distance of the ionic state is smaller than that of the neutral ground state.

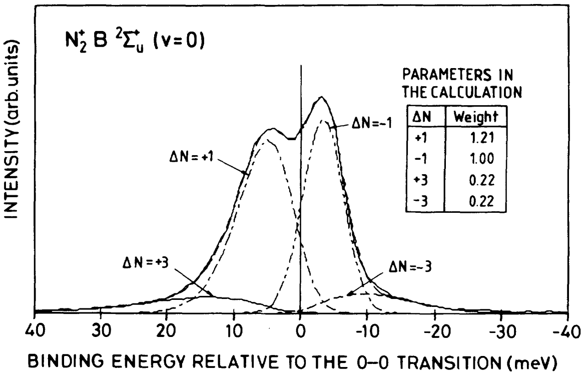

FIG. 3. The experimental (full line) and fitted theoretical (dashed line) $X\,^1\Sigma_g^+(\mathrm{N}_2,\ v=0)\rightarrow B\,^2\Sigma_u^+(\mathrm{N}_2{}^+,\ v=0)$ spectra shown together. The spectra are very similar and an obvious difference can be seen only at -12 meV from the zero level, where the intensity of the experimental spectrum is somewhat higher. For clarity, the subbands corresponding to transitions with $\Delta N=\pm1$ and ±3 are included. Also the weights used in the fitting of the theoretical spectrum are shown in the figure normalized to 1.00 for $\Delta N=-1$ subband. The energy scale refers to zero at the (unobserved) 0-0 transition.

In conclusion, the present study confirms the adopted selection rules for rotational transitions in photoelectron spectra of homonuclear diatomic molecules. The rotational subbands corresponding to transitions involving different ΔN are clearly exhibited in the spectra, which has allowed a determination of the relative intensities of the rotational transitions. The results also show that the electronic structure is far from that derived in a united-atom description, where the $3\sigma_g$ orbital becomes the $3s$ atomic orbital. In the ionization from this orbital, only transitions involving the $\Delta N=0$ would be allowed.

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