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HIGH RESOLUTION VACUUM ULTRAVIOLET SPECTROSCOPY OF SMALL MOLECU--ETC(U)
DEC 77 W H PARKINSON, D E FREEMAN, K YOSHINO F49620-77-C-0010

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HIGH RESOLUTION VACUUM ULTRAVIOLET SPECTROSCOPY OF SMALL MOLECULES

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Instrumentation

The installation and re-optimization of the operating characteristics of the 6.65m McPherson vacuum spectrograph have been successfully accomplished at Harvard College Observatory, and a wavelength resolution of 0.006 Å is achieved in the second order of a grating with 1200 lines per mm. Extensive optical tests on the pair of gratings with 2400 grooves/mm revealed deviations from constant surface curvature which resulted in deterioration of their previously excellent focussing properties and consequent loss of resolution. The original supplier of these gratings, Bausch and Lomb, confirmed these findings and ascribed the defective behavior to distortions of the epoxy substrate of these replica gratings; the distortions which occurred on aging were probably caused by traces of water introduced accidentally during the manufacturing process. Bausch and Lomb have supplied a new pair of 2400 grooves/mm gratings on the existing optical blanks, at no cost.

Photopredissociation of N_2 and its VUV Absorption Spectrum

Predissociation of the N_2 molecule has been studied in absorption in the 840-860 Å region. All of the absorption bands of the $b'(v)\,{}^1\Sigma_u^+ \leftarrow X(0)\,{}^1\Sigma_g^+$ system were found to contain only sharp rotational lines for $v<20$. Rotational lines in the band with $v=19$ are sharp, whereas those in the bands with $v=21$ and 22 are broadened due to predissociation. A detailed study of the band with $v=20$ reveals the existence of sharp and broadened rotational lines in the same band. R(J) branch lines with $J<6$ and P(J) lines with $J<8$ are very sharp but the others are diffuse. This result implies that the lowest rotational level that is predissociated is the F(7) level located 117264.9 cm^{-1} above the ground state $J=0$, $v=0$ level. The dissociation limit $N^2D^o + N^2D^o$ lies 117160 $\pm$ 40 cm^{1-} above this ground state level and almost all of the $\pm$ 40 cm^{-1} uncertainty is in the value of the ground state dissociation energy of N_2. The observed predissociation occurs therefore only 105 $\pm$ 40 cm^{-1} above the $N^2D^o + N^2D^o$ limit. In addition to the diffusiveness noted at high v values in the $b'(v)\,{}^1\Sigma_u^+ \leftarrow X(0)\,{}^1\Sigma_g^+$ band system, diffusiveness is also observed in the Rydberg band $c_5'(1)\,{}^1\Sigma_u^+ \leftarrow X(0)\,{}^1\Sigma_g^+$ whereas the Rydberg band $c_4(1)\,{}^1\Pi_u \leftarrow X(0)\,{}^1\Sigma_g^+$ remains sharp. This suggests that the state causing predissociation is more likely to be a Σ than a Π state.

The first member of the $^1\Sigma_u^+$ Rydberg series of N_2, c_4'-X, has been photographed in absorption below 1000 Å, and a rotational analysis of its (v,o) bands performed for v = 0-4. The weak overlapping (v,o) bands, v = 1-14, of the non-Rydberg transition b'-X are also rotationally analyzed. Irregularities in line spacings, intensity anomalies, and observed variations in excited state rotational constants are interpreted in terms of the homogeneous perturbation $c_4'(v_1)$ x $b'(v_2)$. This interpretation of the $c_4'(0)$ x b'(1) interaction is confirmed by examination of the corresponding bands of $^{15}N_2$, which show small isotopic shifts and exhibit similar perturbations at almost the same energies as for $^{14}N_2$. The identity of both the $c_4'(0)$ and b'(1) states as $^1\Sigma_u^+$ is established, and all the N_2 bands observed in the region studied can be assigned without invoking the presence of a $^1\Pi_u$ state. The $c_4'(0)$ x b'(1) perturbation is very localized, but other perturbations such as $c_4'(4)$ x b'(13), $c_4'(1)$ x b'(4), $c_4'(3)$ x b'(10), and $c_4'(2)$ x b'(7) extend over wider ranges of J and correspond to increasing values of the perturbation matrix element.

Spectroscopy of van der Waals Molecules with Laser Potential

Analyses have been made of the absorption spectra of the rare gas mixtures Xe/X (X = He, Ne, Ar, or Kr) and Kr/Y (Y = He, Ne, Ar, or Xe), which had been photographed at high resolution near each of the first two resonance lines of Xe I and Kr I, respectively, under conditions designed to minimize overlapping absorption by the symmetric dimers Xe_2 or Kr_2. The overall formation of spectral features near a resonance line is predominantly towards short wavelengths, and the degree to which discrete bands form near a resonance line generally increases with increasing atomic weight of X or Y. Properties of the heteronuclear van der Waals molecules XeX and KrY are inferred from the spectra which are given partial interpretations in terms of transitions from the bound ground electronic state (Ω = 0) to bound or free excited electronic states (Ω = 0, 1). Bound excited electronic states are found for KrXe near the first resonance levels of XeI and KrI, and for KrXe and ArXe near the second resonance level of XeI.

Publications

K. Yoshino and Y. Tanaka, High resolution VUV absorption spectrum of N_2: Homogeneous perturbation between c_4' (0) $^1\Sigma_u^+$ and b' (1) $^1\Sigma_u^+$ levels, J. Mol. Spectrosc. 66, 219-232 (1977).

D.E. Freeman, K. Yoshino, and Y. Tanaka, Vacuum ultraviolet absorption spectra of binary rare gas mixtures and the properties of heteronuclear rare gas van der Waals molecules, J. Chem. Phys. (submitted in May 1977 and accepted for publication).

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A 6.65 metre vacuum spectrograph has been installed and a wavelength resolution of 0.006 Å attained. Absorption spectra of N_2 below 1000 Å have been rotationally analyzed, and homogeneous perturbations identified; rotational line broadening in certain bands indicates the presence of predissociation at about 105 cm^{-1} above the $N_2^2D+N_2^2D$ dissociation limit. The absorption spectra of binary rare gas mixtures have been photographed and interpreted in terms of transitions within van der Waals molecules, from their bound → next page

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20. ABSTRACT (Continued)

ground electronic states to bound or free excited electronic states near the first and second atomic resonance levels of xenon and krypton.