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HIGH RESOLUTION VUV MATRIX ISOLATION SPECTROSCOPY USING SYNCHROTRON RADIATION: N_2 in Ne

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High Resolution VUV Matrix Isolation Spectroscopy using Synchrotron Radiation: N_2 in Ne

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Abstract

We have investigated the VUV absorption spectrum of nitrogen in a neon matrix exploiting the intense synchrotron radiation continuum of the storage ring DORIS and the high resolving power of a 3 m normal incidence monochromator. With an improved sample preparation technique we were able to observe both the allowed transitions b $^1\Pi_u$ and b $^1\Sigma_u^+$ between 12.4 and 14.0 eV and even the forbidden transitions w $^1\Delta_u$ and a $^1\Pi_g$ between 8.0 and 11.0 eV. All four transitions consist of long progressions of sharp bands ($\Gamma \sim$ 10 meV) which are deperturbed in the matrix due to the suppression of nearby Rydberg states. Using symmetry arguments, our analysis of the spectra leads us to the conclusion that the N_2 molecule is oriented along the (1, 1, 1) direction in the host lattice. A detailed fine structure is observed for most bands for the first time. This fine structure is caused by dynamical interactions of the excited molecules with the matrix and is interpreted as excitation of librational modes of the N_2 molecule and a selective coupling to phonon modes of the neon lattice.

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Introduction

Matrix isolation spectroscopy developed in the Infrared and Visible has recently attracted interest also in the vacuum ultraviolet (VUV) region. Many of the traditional problems in the VUV have been overcome by the use of high intensity continuous light sources. Synchrotron radiation, in particular, has made quantitative high resolution matrix isolation spectroscopy possible {1}.

In the VUV one is able to study the influence of the matrix environment to a molecule in the electronic ground and the electronically excited states. These influences manifest themselves in static interactions (deperturbations, changes of oscillator strength, solvent shifts) and in side bands which show explicitly the dynamic interactions (librational modes, phonon excitations). The system nitrogen in neon was chosen for our experiments, because the electronic states of nitrogen are well known from gas {2, 3} and solid phase {4,5} measurements and neon is a matrix which is transparent over a large energy range up to $\sim$ 18 eV. Further, neon exhibits only small interactions with the N_2 molecule so that the matrix spectra are similar to those in the gas phase. The specific differences will be discussed in the following sections.

Results

(1) Forbidden transitions to a $^1\Pi_g$ and w $^1\Sigma_u$

The transitions a $^1\Pi_g \leftarrow X\ ^1\Sigma_g^+$ and w $^1\Delta_u \leftarrow X\ ^1\Sigma_g^+$ are both electric dipole forbidden in the gas phase. The oscillator strength is therefore small and extremely thick samples are needed to observe these transitions. Fig. 1 shows the absorption spectrum of a 2 mm thick neon layer doped with 1% N_2 in the region from 8.5 to 11.5 eV. Both transitions are to be seen as long progressions with sharp bands. In the gas phase, the transition to a $^1\Pi_g$ is allowed in magnetic dipole radiation, the w $^1\Delta_u$ transition is not allowed even in quadrupole radiation and therefore the oscillator strength of the latter is more than 10^3 times smaller than that for the a $^1\Pi_g$ transition [2]. In the matrix, the two transitions have approximately the same intensity. Consequently, the local symmetry of the N_2 molecule at a lattice site must have changed in such a way that the transition to w $^1\Delta_u$ becomes allowed. This is only possible for a local D_{3d} symmetry equivalent of an orientation of the N_2 molecule along the (1, 1, 1) direction in the neon fcc-lattice [6]. Thus, we take the relative high intensity of the w $^1\Delta_u$ transition as a strong argument in favor of such an orientation. Further, we note that the difference between the excitation energies in the matrix and in the gas phase is only 13 meV which shows the small interaction of these states with the neon host matrix.

(2) Allowed transitions to b $^1\Pi_u$ and b $^1\Sigma_u^+$

The progressions of these two valence transitions are shown in Fig. 2. In the gas phase, they are strongly perturbed by the nearby Rydberg transitions so that they form a very irregular progression. These perturbations have been measured quantitatively [3] and described theoretically by deperturbation calculations [7].

In the matrix, the progressions are regular without a perturbation (Fig. 2). The Rydberg orbitals have such a large extension that they are suppressed in the matrix. Therefore, they do not perturbe the valence transitions. A comparison of the energy values in the matrix derived from our measurements and those from deperturbation calculations [7] shows a very close correspondence. This is on one hand a proof of the quality of the calculations and on the other hand it manifests the hypothesis that fixing a molecule in a matrix is a reasonable method for the deperturbation of a valence transition. The spectroscopic information concerning these progressions will be discussed in detail elsewhere [8].

(3) Fine structure of the bands

Our results obtained with carefully prepared samples show sharp bands with a detailed fine structure for most of the nitrogen bands in the neon matrix. This is in contradiction to previous measurements for this system [9, 10]. The fine structure is due to dynamic interaction of the excited molecule with the matrix. In

Fig. 3, as an example, the fine structure of the band a $^1\Pi_g$, v' = 0 is shown. On the low energy wing, the zero phonon line (ZPL) is to be seen. It represents the pure electronic transition. The next two peaks at 1.4 and 2.8 meV are building a progression of a librational mode of the N_2 molecule. The maximum 4 meV above the ZPL is due to the excitation of the transverse acustical phonons of the neon lattice. The longitudinal phonon branch does not couple with this particular excitation [1]. A similar result was found by Boursey et al. for NO in neon [11]. In order to understand this selective coupling to a particular phonon branch, one has to determine the phonon density of states for a neon lattice perturbed by excited N_2 molecules. This density strongly depends on the symmetry of the excited states of the guest molecule. Thus, for example, the b $^1\Sigma_u^+$ state was found to couple only with the longitudinal acustical phonon branch of the host. Further, theoretical investigations concerning the observed fine structure and the selective coupling to the phonons of the matrix would be of great interest.

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References

1 P. Gürtler, Thesis Universität Hamburg (1979)

2 G. Herzberg
Molecular Spectra and Molecular Structure
Vol. I, Spectra of Diatomic Molecules
Van Nostrand Reinhold Co., New York 1950

3 P. Gürtler, V. Saile, E. E. Koch, Chem. Phys. Letters 48, 245 (1977)

4 e.g. R. Haensel, E. E. Koch, N. Kosuch, U. Nielsen and M. Skibowski, Chem. Phys. Letters 9, 548 (1971)

5 E. Boursey, V. Chandrasekharan, P. Gürtler, E. E. Koch, P. Kunsch, and V. Saile, Phys. Rev. Letters 41, 1516 (1978)

6 R. E. Miller, J.D. Decius, J. Chem. Phys. 59, 4871 (1973)

7 M. W. Leoni, Thesis Eidg. Techn. Hochschule Zürich (1972)

8 P. Gürtler et al. to be published

9 E. Boursey, J.Y. Roncin, Phys. Rev. Lett. 26, 308 (1971)

10 B. Drerup, J. Hormes, M. Sauer, R. Scullman, Chem. Phys. Lett. 61, 370 (1979)

11 E. Boursey, J.Y. Roncin, J.Mol. Spec. 55, 31 (1970)

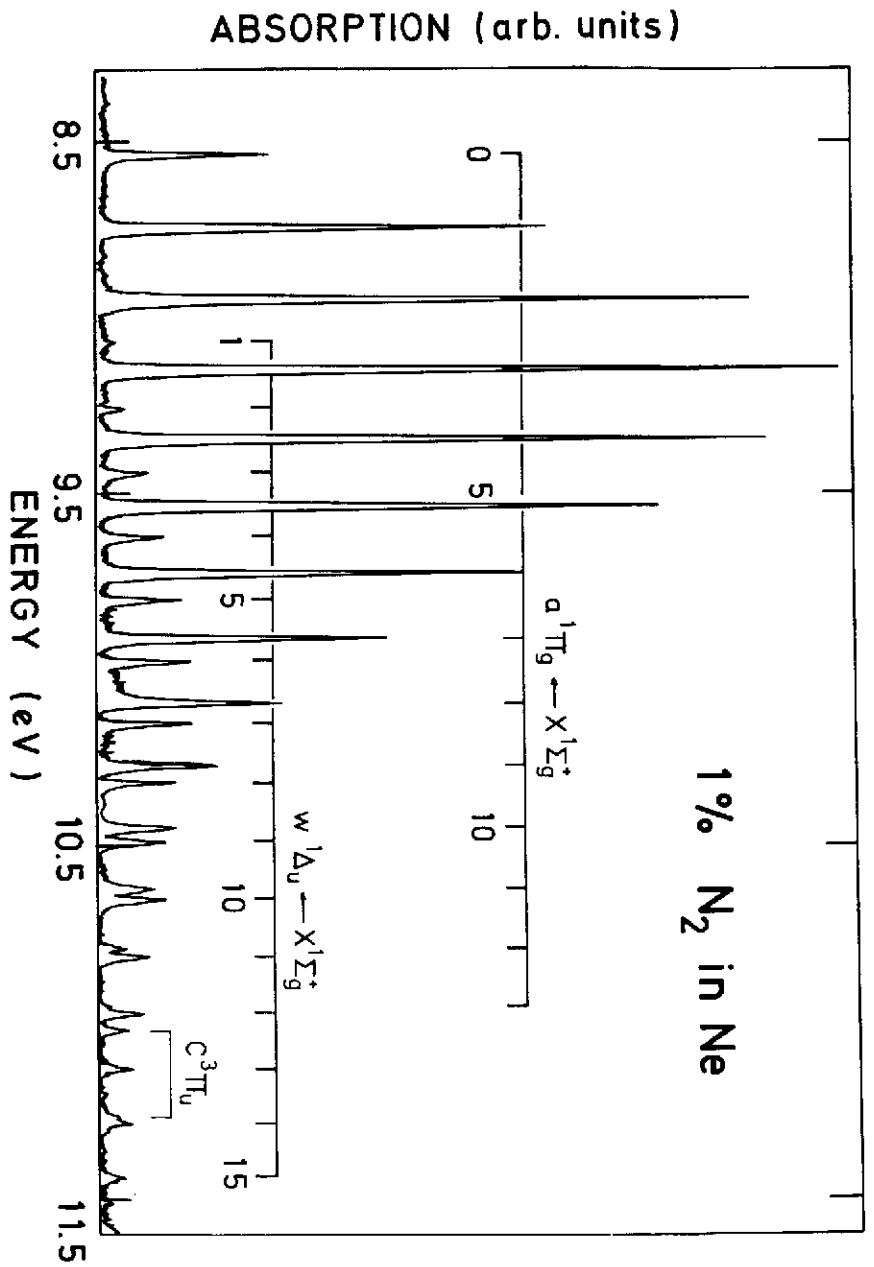
Figure Captions

Fig. 1 Absorption spectrum of N_2 in a neon matrix in the region of the forbidden transitions a $^1\Pi_g \leftarrow X\ ^1\Sigma_g^+$ and w $^1\Delta_u \leftarrow X\ ^1\Sigma_g^+$. The singlet-triplet transition C $^3\Pi_u \leftarrow X\ ^1\Sigma_g^+$ observed for the first time is indicated too.

Fig. 2 Absorption spectrum of N_2 in a neon matrix in the region of the allowed transitions b $^1\Sigma_g^+ \leftarrow X\ ^1\Sigma_g^+$ and b $^1\Sigma_u^+ \leftarrow X\ ^1\Sigma_g^+$.

Fig. 3 Fine structure of the 0 - 0 band of the transition a $^1\Pi_g \leftarrow X\ ^1\Sigma_g^+$. ZPL denotes the zero phonon line.

Fig. 1



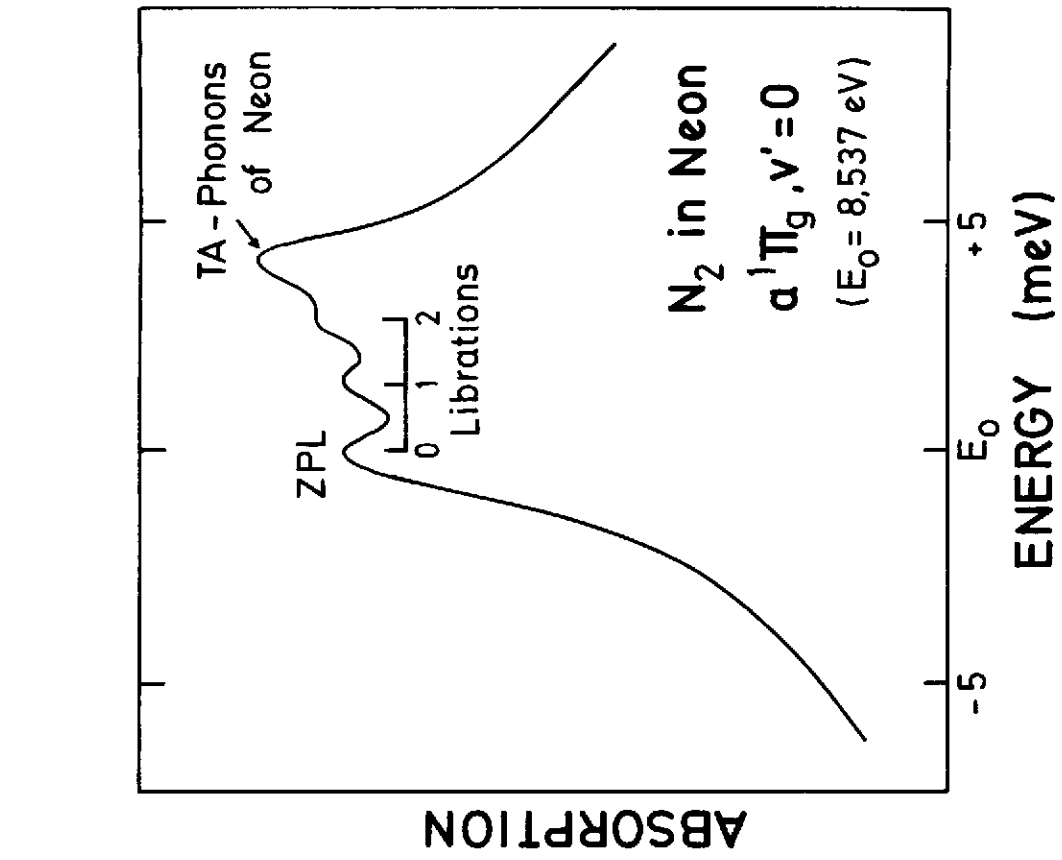

ABSORPTION
ENERGY (meV)
+5
E0
-5
N2 in Neon
a 1Πg, v'=0
(E0= 8,537 eV)
TA-Phonons of Neon
ZPL
0 1 2
Librations

Fig. 3

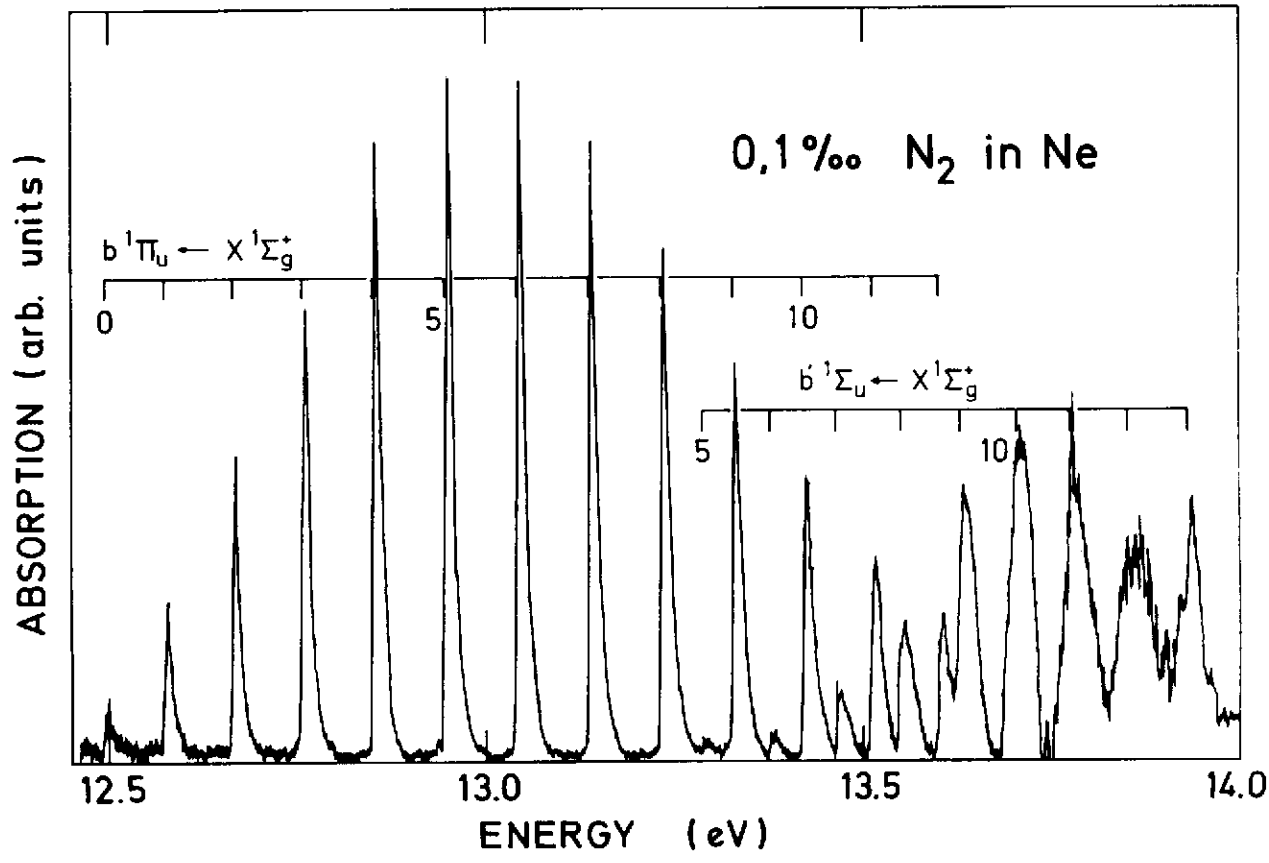

ABSORPTION (arb. units)
0,1‰ N2 in Ne
b 1Πu ← X 1Σg+
0
5
10
b' 1Σu ← X 1Σg+
5
10
12.5
13.0
13.5
14.0
ENERGY (eV)

Fig. 2