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Vacuum Ultraviolet Reflectivity of Solid Nitrogen and Oxygen

by

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Vacuum Ultraviolet Reflectivity of Solid Nitrogen and Oxygen[≠]

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The reflectance of solid nitrogen and oxygen has been measured at a 15° angle of incidence from 10 to 23 eV at temperatures below 10° K using snychrotron radiation. The observed transitions are compared to molecular excitations.

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Ultraviolet absorption and energy loss measurements on gaseous nitrogen[1,2,3] and oxygen[4,5,6] have been performed for many years. The complex structure of these spectra has been interpreted as being due to several Rydberg series of the diatomic molecules. Recently Buxton and Duley[7] investigated the optical properties of solid nitrogen in the VUV-range by measuring the reflectivity at a 45° angle of incidence using a photographic method. No measurements have, as yet, been reported for solid oxygen in this energy region.

In this paper we are going to give a report on results of reflectivity measurements of solid nitrogen and oxygen at a 15° angle of incidence up to 23 eV using photo-electric detection. The continuum of the synchrotron radiation of the Deutsches Elektronen-Synchrotron DESY[8] was monochromatized by a normal incidence monochromator[9]. The spectral resolution of the monochromator was about 2 Å over the whole energy range. The gases (L'Air Liquide, 99.9992 % purity) were evaporated as thin films onto a LiF or KBr single crystal which were cooled in a He-cryostat below 10° K. In the case of oxygen only LiF was used. During evaporation reflectivity oscillations due to interference were monitored at a fixed energy below 10 eV where the solid gases are transparent. When the oscillations ceased evaporation was stopped. The light reflected from the film surfaces at an angle of incidence of 15° was detected with an open multiplier Bendix 306. Cryostat and multiplier were mounted into an ultra-high vacuum system[10] which was baked for several hours at 150° C before the experiments which were then performed at a basic chamber pressure in the order of 10^{-9} Torr. The technique we used was the same as the one used in the reflection studies on solid rare gases.[11]

The reflection spectra of N_2 are shown in Figs. 1, 2 and of O_2 in Fig. 3. The absolute energy positions of the peaks are accurate wihtin ±2 Å, i.e. 0.016 eV at 10 eV, the relative distances from peak to peak are more accurate, namely ±1 Å. The reflectance I/I_o is given in arbitrary units for both cases since the reflected intensity I and the incident intensity I_o were not measured simultaneously. The spectral behaviour of I_o, however, was well known. The relative heights were reproducible within 10 % over the whole spectrum, the internal consistency of the relative heights of the different peaks is better than 5 %.

Nitrogen

Figure 1 shows the results for nitrogen between 10 and 23 eV, Fig. 2 the vibrational structure at 13 eV in an extended scale. In Fig. 2 we have added in brackets the positions of the sharp maxima as measured by Buxton and Duley[7]. The agreement of the peak positions is excellent, although the overall shape is somewhat different. We assign these peaks, as did Buxton and Duley, to the vibrational levels of the N_2-molecular band $b^1\Pi_u$. Compared to the vapour phase the centre of this band is not shifted and even the vibrational spacing of about 90 meV is preserved. The reflectance drops markedly at 15 eV and weaker peaks follow at 16.5 eV and 19.2 eV. There are significant differences in this energy range between our measurements and those reported by Buxton and Duley, as can be seen from Fig. 1. Relative to the band at 13 eV their reflectance values above 15 eV are higher by a factor of about three as compared to our measurements. Furthermore, there is no agreement in the peak positions. These differences may be explained by the experimental arrangement: different angles of incidence and different recording techniques.

Tentatively, we ascribe the peaks above 15 eV to interband transitions which originate from levels of the N_2 molecule lying above the first ionization limit (15.58 eV)[2]. The 16.5 structure would then be due to the bands formed by the states of the Worley's series ($\sim$ 16.9 eV)[1], whereas the 19.2 eV peak may have its origin from states of the Hopfield series ($\sim$ 19 eV)[1]. Due to the overlap of molecular bands in these series and their weakness one cannot expect that they be preserved as separate lines in the solid.

Weak structure below 12 eV consisting of a great number of lines was found when N_2 was evaporated on a LiF single crystal. This structure was fairly reproducible several times using films of different thickness. The spectra of Buxton and Duley also show two weaker structures below the onset of the $b^1\Pi_u$ vibrational level. We could not find this structure, however, when KBr was used as a substrate. Up to now we cannot explain this.

Oxygen

Figure 3 shows the reflection of solid oxygen. In contrast to solid N_2 no sharp lines originating from vibrational levels were observed. The spectrum consists mainly of three broad maxima, all of the same order of magnitude, in contrast to solid N_2. This different behaviour may be roughly understood by the differences of the gas spectra: the series in O_2 overlapp each other, whereas in N_2 the $b^1\Pi_u$ series is well separated from others. The intensities of the different excitations are of the same order of magnitude over the whole energy region for O_2, whereas for N_2 the intensity at 13 eV is about three times higher as compared to the other parts of the spectrum. The shoulder at 12 eV in the solid is correlated to the $O_2^+, X^2\Pi_g$ transitions at $\sim$12.1 eV in the gas[1]. The prominent reflectance maximum at 14.25 may ori-

ginate from the strong vibrational levels between 12 - 15 eV observed in the gas[6]. The shoulder at 15.75 eV is ascribed to the $O_2^+, a^4\Pi_u$ band at 16.1 eV[5,6], the maximum at 17 eV to the $O_2^+, a^2\Pi_u$ configuration at 16.82 eV[5]. Finally, the maximum at 18.4 eV may be correlated to the Rydberg series $(O_2, X^3\Sigma_g^- \rightarrow O_2^+, b^4\Sigma_g^-)$, terminating at 18.3 eV[4,5,6].

Acknowledgment

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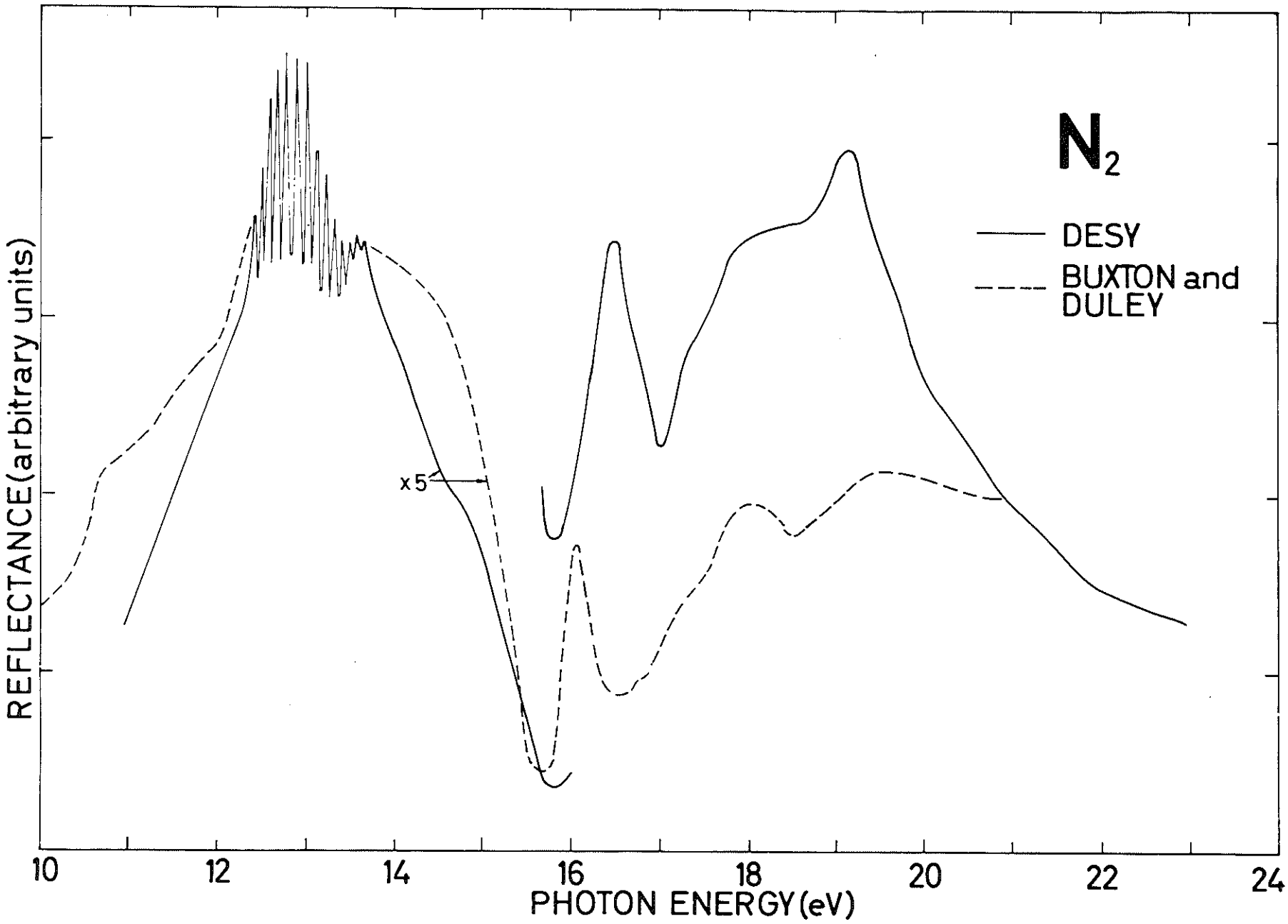
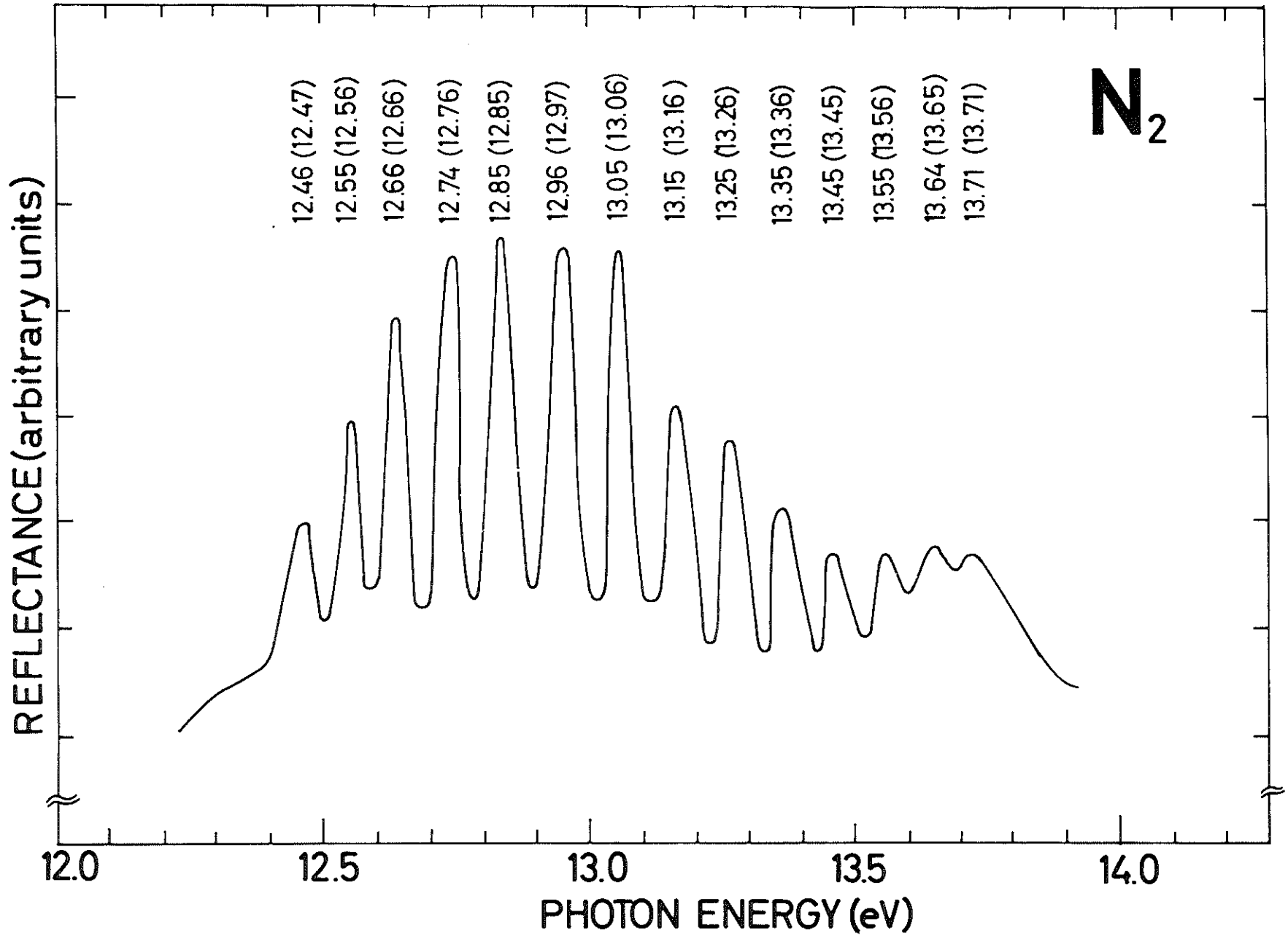
Figure captions

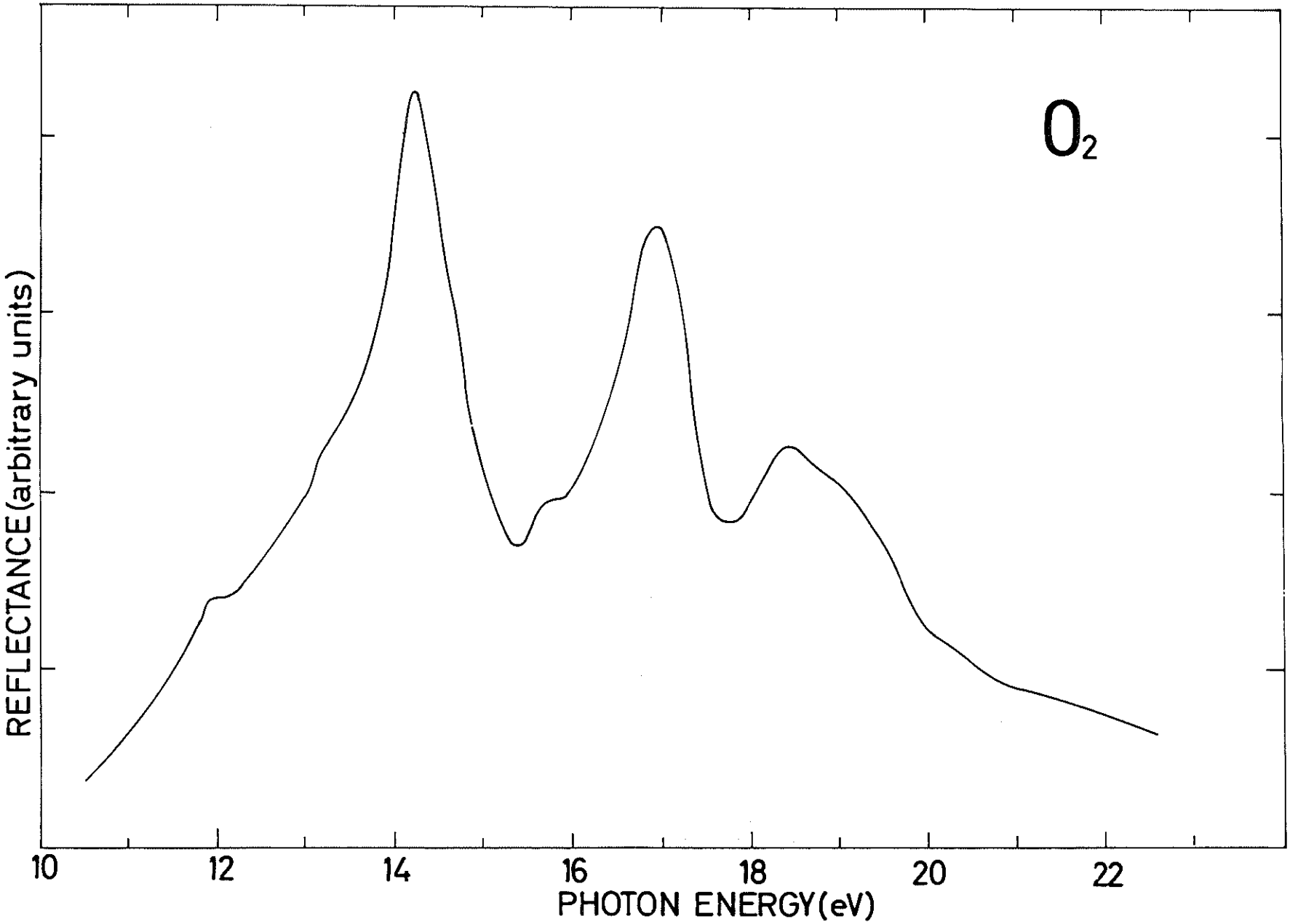
Fig. 1 Reflectance of solid N_2 at 10° K for an angle of incidence of 15° (solid line). The dashed line gives Buxton and Duley's reflection curve for an angle of incidence of 45° (Ref. 7); for clarity the line series has been omitted.

Fig. 2 Reflectance of solid N_2 at 10° K for an angle of incidence of 15°, showing the $b^1\Pi_u$ vibrational levels. The values given by Buxton and Duley (Ref. 7) are added in brackets.

Fig. 3 Reflectance of solid O_2 at 10° K for an angle of incidence of 15°.


N2
DESY
BUXTON and DULEY
x5
REFLECTANCE (arbitrary units)
PHOTON ENERGY (eV)
10
12
14
16
18
20
22
24


12.46 (12.47)
12.55 (12.56)
12.66 (12.66)
12.74 (12.76)
12.85 (12.85)
12.96 (12.97)
13.05 (13.06)
13.15 (13.16)
13.25 (13.26)
13.35 (13.36)
13.45 (13.45)
13.55 (13.56)
13.64 (13.65)
13.71 (13.71)
N2
REFLECTANCE (arbitrary units)
12.0
12.5
13.0
13.5
14.0
PHOTON ENERGY (eV)


O_2
REFLECTANCE(arbitrary units)
10
12
14
16
18
20
22
PHOTON ENERGY(eV)