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Electronic Excitation of Solid Carbon Dioxide in the Extreme Ultraviolet[+]

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The reflection spectrum of solid CO_2 has been measured for 30 K at 15° angle of incidence from 10 to 30 eV using synchrotron radiation. The ε_2-spectrum was calculated by means of the dispersion relation. The observed electronic absorption bands are compared to molecular excitations.

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The optical excitation of solid CO_2 has not yet been studied in the extreme ultraviolet region. Considering the absorption of gaseous CO_2 (1) strong electronic excitation was expected to start in the solid only above 10 eV. At these energies, the strong Price-Simpson Rydberg series with vibrational progressions which converge to the first ionization limit of CO_2 at 13.79 eV (corresponding to a molecular transition $^1\Sigma_g^+ \rightarrow {}^2\Pi_g$) occur in the gaseous phase. This energy range is difficult to reach with conventional light sources. Furthermore, simple absorption technique becomes difficult in the case of solids in the range above the LiF cutoff because of the lack of transparent substrates.

Reflection spectroscopy has recently been shown to be a very useful tool for the study of the electronic excitation of solid gases in the vacuum ultraviolet (2, 3). Especially in connection with the use of synchrotron radiation many new excitations were found in the extreme ultraviolet (2, 4, 6b). Particularly the properties of the solid rare gases Ne (4), Ar (2), Kr (2, 5), Xe (2, 3, 5) have been studied by the reflection method, more recently also the main components of the atmosphere N_2 and O_2 (6) and some organic compounds (7). In this paper we report our first results of a study of the optical excitation of solid CO_2 in the extreme ultraviolet.

The reflectivity was measured at 15° angle of incidence for photon energies between 10 and 30 eV using the intense continuum of the synchrotron radiation from the Deutsches Elektronen-Synchrotron DESY (8). The experimental arrangement is shown in Fig. 1. A special normal-incidence monochromator was used (9). Its spectral resolution was 2 Å over the whole energy range. The wavelength calibration was exact within ±2 Å, i.e. ±15 meV at 10 eV. The gases (purity 99.995 %) were evaporated as thin films onto gold as a substrate which was

cooled down to 30 K in a He cryostat. The evaporation was stopped when intensity oscillations arising from interference effects due to changes in film thickness were no longer observed. The reflected light was detected with an open magnetic multiplier. Cryostat and multiplier were mounted into an ultra-high vacuum system which was baked for several hours at 150° C. By this procedure 10^{-9} Torr was obtained before cooling. Surface contamination was negligible during the experiment.

Figure 2 represents the experimental results with the calculated imaginary part of the dielectric constant, ε_2. The latter quantity was obtained by Kramers-Kronig analysis of the reflection data assuming a decrease of the reflection with E^{-4} above 30 eV and a somewhat arbitrary monotonic decrease below 10 eV, the reflectivity finally fitting to R = 1 % at zero energy. The latter value corresponds to the optical real index of refraction n = 1.22 (10). The weak broad band observed in the gas between 7 and 10 eV (1) will probably also show up in a modified form in the reflection spectrum. Its contribution was assumed to be negligible in calculating ε_2. Because of the above extrapolation procedure and inaccuracies which might be present in the determination of the absolute reflectance, the ε_2-values may be improvable. Especially the value for the first peak at about 10.6 eV may be strongly affected by the extrapolation to lower energies. Figure 1 demonstrates that the reflection and the ε_2-spectrum are very similar. Only small shifts concerning energy and magnitude are observed. It should be noted that slight shifts in the spectral behavior and changes in the absolute reflectivity value were observed when the temperature or speed of evaporation were varied. These effects have to be studied more carefully in the future.

Strong electronic excitation starts at about 10 eV as expected from observations in the gaseous phase. The spectrum is characterized by four strong broad bands. The reflection maxima are located at about 10.6, 13.1, 14.9 and 21.2 eV. They are accompanied by additional fine structure. No isolated Rydberg bands with vibrational progressions are observed as, for instance, in solid N_2 at about 13 eV (6). They are apparently all smeared out under the influence of the crystal field. The observed broad bands are correlated to those found by excitation of solid CO_2 with fast electrons (11). In the reflection spectra, however, much more fine structure is observed, probably due to the better energy resolution.

With regard to energy position and relative oscillator strength the bands cannot be directly assigned to the absorption bands in gaseous CO_2. In the gas phase four different partially overlapping groups of bands superimposed on a broader continuum are observed between 10 and 20 eV. These are the Price-Simpson Series converging to 13.79 eV ($^2\Pi_g$), the Tanaka-Ogawa-Series converging to 17.32 eV ($^2\Pi_u$), the Hennings series with an ionization limit of 18.08 eV ($^2\Sigma_u^+$) and further series with a limit at 19.38 eV ($^2\Sigma_g^+$) (1,12). They all correspond to the excitation into Rydberg orbitals and the final removal of electrons from the four outermost molecular orbitals of the ground state configuration of the CO_2-molecule:

$$\ldots\ldots (4\sigma_g)^2 \; (3\sigma_u)^2 \; (1\pi_u)^4 \; (1\pi_g)^4 \;, \qquad {}^1\Sigma_g^+$$

By taking an average of the fine structure of the gaseous absorption spectra one obtains centers for absorption which are, indicated by arrows in Fig. 2. A shift of about 1 eV to lower energies has to be assumed to make the averaged spectra of the gas roughly coincide with the solid state spectra concerning energy. A speculation that such shifts and the broadening can be simply ex-

plained as being due to the crystal field potential has to be checked quantitatively by theoretical investigations.

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Figure Captions

Fig. 1 Sketch of the experimental set-up

Fig. 2 Reflection spectrum (R (%), solid line) and the imaginary part of the dielectric constant ε_2 (dashed line) of solid CO_2 between 10 and 30 eV. The dash-dotted lines below 10 eV indicate the extrapolation to lower energies. The arrows indicate the approximate centers of the averaged absorption bands in gaseous CO_2.

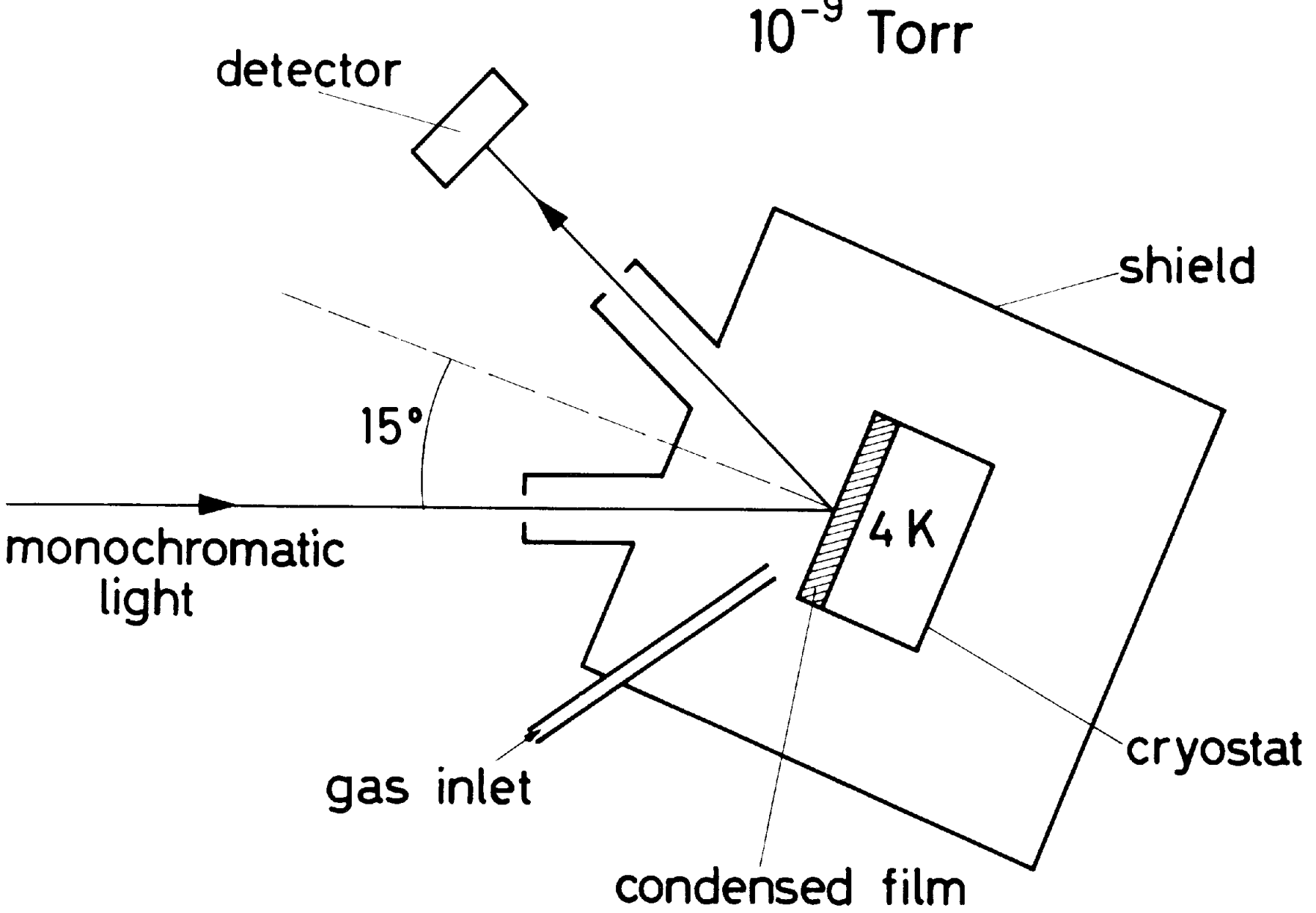
10^{-9} Torr
detector
shield
15°
monochromatic
light
4 K
cryostat
gas inlet
condensed film

Fig. 1

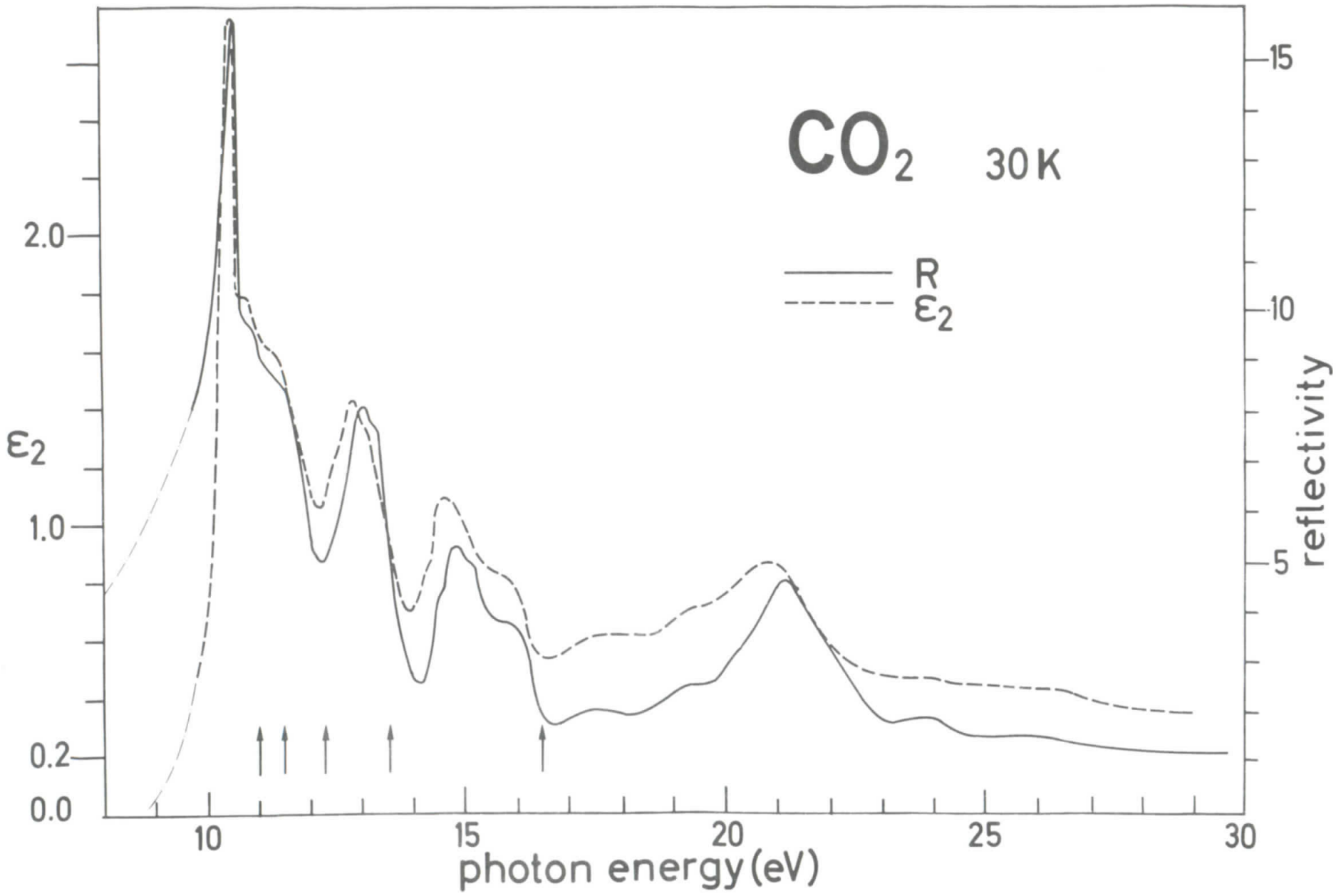
CO2 30 K
R
ε2
ε2
2.0
1.0
0.2
0.0
15
10
5
reflectivity
10
15
20
25
30
photon energy (eV)

Fig. 2