Infrared and Electronic Spectra of Matrix-isolated Dichlorodioxo- and Dibromodioxo-molybdenum(VI) and -tungsten(VI)

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The prominent i.r. and u.v.–visible bands of the title compounds isolated as monomers in low-temperature matrices have been obtained and assigned. For MoO_2Cl_2 and MoO_2Br_2, the vibrational isotope effect on the antisymmetric stretching mode ν(Mo=O) leads to estimates of bond angles OMoO of 109 ± 3°, whilst for WO_2Cl_2 and WO_2Br_2, relative band intensities predict OWO = 107 ± 2° for both molecules. In the quantitative assignment of the electronic spectra, it is suggested that the positions of the charge transfer bands require somewhat lower values of $\chi_{opt.}$ than are appropriate for octahedral complexes.

There are six known dioxide dihalides of molybdenum and tungsten. These are MoO_2F_2, MoO_2Cl_2, MoO_2Br_2, WO_2Cl_2, WO_2Br_2, and WO_2I_2,[1] and in addition, there is mass spectrometric evidence for WO_2F_2.[2] A combination of *X*-ray diffraction and vibrational spectroscopy has established that the solid-phase structures of the chloro- and bromo-compounds involve distorted octahedral co-ordination of the transition metal, with oxygen bridging,[3–7] whilst i.r. data on solid MoO_2F_2 suggest both oxygen and fluorine bridging.[4] The structure WO_2I_2 is uncertain. In the vapour phase, a variety of mass spectrometric, i.r., and Raman studies have been interpreted in terms of *monomeric* (C_{2v}) species, but apart from one electron diffraction report on MoO_2Cl_2,[8] no structural data are available. Similarly, very little is known of their molecular electronic absorption spectra, although the chromium analogues, CrO_2F_2 and CrO_2Cl_2, have been extensively studied.[9–11] A gas-phase He–I photoelectron spectrum has, however, been reported for MoO_2Cl_2.[12]

At the present time, there is considerable interest in these compounds in view of their importance in high-temperature vapour transport (for example, in incandescent lamps [13]) and we are currently studying a number of such systems in detail in order to characterise these species more completely. In our earlier paper [14] on MOX_4 monomers (M = Mo or W; X = F, Cl, or Br) we reported high resolution i.r. and electronic spectral data obtained from matrix studies, and demonstrated that this experimental technique offered a significant advanrage over conventional vapour-phase methods in terms of spectral resolution. This present paper describes a similar series of experiments on monomeric MO_2X_2 species (M = Mo or W, X = Cl or Br), and in addition to reporting their electronic spectra for the first time, we also demonstrate how the use of isotope fine structure and relative band intensities in the i.r. can lead to estimates of interbond angles.

Experimental

Preparation of Compounds.—Dichlorodioxomolybdenum(VI) was prepared by the reaction between MoO_3 and $MoCl_5$ in a sealed tube, following the method of Glukhov and Eliseev,[15] whilst MoO_2Br_2 was obtained from the reaction between MoO_3 and BBr_3 in a similar manner to that described earlier for $WOBr_4$.[14] The tungsten analogues, WO_2Cl_2 and WO_2Br_2, were prepared in two ways. The first of these was based on the reaction between WO_3 and the appropriate carbon tetrahalide in a flow system as described by Castro Luna and Rivarola.[16] Although the principal product of this reaction was the desired WO_2X_2 species, some contamination by the corresponding WOX_4 species was generally present, and this required careful separation by vacuum sublimation. A second, novel, synthesis was therefore sought based on the reaction between WO_3 and molten alkali-metal halides. This route to oxohalide species was chosen in view of its success in the preparation of related oxohalide anions,[17,18] and in our systems, the use of LiBr/KBr and LiCl/KCl melts allowed us to carry out the reactions in Pyrex.

In a typical synthesis, a sample of WO_3 (*ca.* 0.5 g) was mixed with an excess of a finely ground, dried, eutectic mixture of either LiBr/KBr (mol ratio 3 : 2, m.p. 340 °C) or LiCl/KCl (mol ratio, 3 : 2, m.p. 360 °C) and gently warmed *in vacuo*. The mixture was then heated to *ca.* 380—400 °C for 2 h under dynamic vacuum during which time the desired product (yellow WO_2Cl_2 or brown WO_2Br_2) sublimed onto the cooler parts of the apparatus. Subsequent elemental analysis indicated that WOX_4 species were not produced in these reactions. Further experiments showed that MoO_2Br_2 could also be satisfactorily produced by this route.

Samples of WO_3 and MoO_3 were freshly prepared as described previously.[14] $MoCl_5$ was obtained from Aldrich Chemical Co. Ltd., and other standard reagents [CCl_4, CBr_4, LiBr, KBr, KCl, $LiCl\cdot 2H_2O$] were obtained from BDH.

All the compounds were resublimed *in vacuo* immediately before use and had satisfactory halogen analyses (calculated values in parentheses): MoO_2Cl_2 [Cl, 35.45 (35.65)], MoO_2Br_2 [Br, 55.45 (55.55)], WO_2Cl_2 [Cl, 24.35 (24.75)], and WO_2Br_2 [Br, 41.45 (42.55)%].

Matrix-isolation Spectroscopy.—Samples were vaporised from Pyrex break-seal ampoules and co-condensed with the appropriate matrix gas (argon or nitrogen; B.O.C.) onto cooled (*ca.* 12 K) spectroscopic windows as described previously.[14] For i.r. studies the spray-on temperatures of the samples (MoO_2Cl_2, 25 °C; MoO_2Br_2, 200 °C; WO_2Cl_2, 300 °C; WO_2Br_2, 300 °C) were higher than those required for u.v.–visible studies (20, 120, 250, and 250 °C respectively) because of the lower absorption coefficients of the i.r. bands. In both types of experiment, estimated matrix ratios were well in excess of 1 000 : 1. The spectrometers and matrix equipment used were as described previously.[14]

Results and Discussion

Infrared Studies.—Previous vibrational studies on vapour-phase MO_2X_2 systems (M = Mo or W, X = Cl or Br) have been interpreted on the basis of tetrahedral C_{2v} monomers,[19–23] and mass spectrometric studies have similarly demonstrated the predominance of monomers.[24] As in our earlier paper [14] on MOX_4 systems, therefore, the main reasons for carrying out matrix-isolation i.r. studies were firstly to establish beyond

Table 1. (*a*) Vibrational fundamentals (cm^{-1}) for monomeric MO_2X_2 species

		MoO_2Cl_2							MoO_2Br_2						WO_2Cl_2				WO_2Br_2		
Mode	Ref.	19	7	20	21	4	22	*a*	19	7	20	21	22	*a*	7	20	23	*a*	20	23	*a*
A_1	ν(M=O)		996	994		996	996	996	995	993	991		995	991	984	992		1 014	985		1 009
B_1	ν(M=O)	972	972	972		966	970	968	969	967	969	970	970	963	972	978		974	973		969
A_1	ν(M−X)		437	437		432	429	434				260	262	262						259	258
B_2	ν(M−X)	450	453	450	450	470	470	451				340	338	351			431	425		305	309
A_1	δ(MO_2)				340	339	338	340					378	378			340			357	363
A_1	δ(MX_2)					113	167						147								
B_1	ρ(MO_2)					211	*ca.* 202						184								
B_2	ρ(MX_2)				280	267	180						161								
A_2	τ					194	116						82								

(*b*) Isotope fine structure [b] for ν(Mo=O) (B_1) in MoO_2Cl_2 and MoO_2Br_2

	^{92}Mo	^{94}Mo	^{95}Mo	^{96}Mo	^{97}Mo	^{98}Mo	^{100}Mo
MoO_2Cl_2	972.1	970.2	969.2	968.2	967.4	966.5	964.7
MoO_2Br_2	966.9	964.9	964.0	963.0	962.2	961.3	959.4

[a] This work, nitrogen matrices. [b] Nitrogen matrices; frequency accuracy ±0.2 cm^{-1}.

doubt the principal i.r. bands of the monomers, to use these data to estimate bond angles, and finally, to select suitable conditions for obtaining u.v.–visible spectra.

The molecular vibrations for a tetrahedral C_{2v} species MO_2X_2 may be shown to be $\Gamma_{vib.} = 4A_1 + A_2 + 2B_1 + 2B_2$, with $\Gamma_{M=O(str.)} = A_1 + B_1$, and $\Gamma_{M-X(str.)} = A_1 + B_2$. Several authors have made partial assignments for the four species considered here, and Table 1 summarises the relevant data. In particular, it is evident that MoO_2Cl_2 has attracted most interest, but even here there is some disagreement over the location of the bending fundamentals. The other three molecules, MoO_2Br_2, WO_2Cl_2, and WO_2Br_2, have received much less attention, and the only basis here for a comparable assignment comes from the Raman study on MoO_2Br_2 by Kovba and Maltsev.[22]

Our matrix-isolation experiments on MoO_2Cl_2, MoO_2Br_2, and WO_2Br_2 gave spectra entirely consistent with the isolation of monomeric species. The frequencies observed in nitrogen and argon matrices rarely differed by more than 2 cm^{-1}, and our nitrogen values are included in Table 1. In the case of WO_2Cl_2, however, we routinely observed two additional features at 1 032 and 380 cm^{-1} (nitrogen matrices) which could be assigned [14] to matrix-isolated $WOCl_4$. These bands were found in all spectra, irrespective of sample history, and we believe they arise from vapour-phase disproportionation of WO_2Cl_2 to give $WOCl_4$ and an (involatile) oxide of tungsten. The presence of $WOCl_4$ as a persistent impurity in vapour-phase studies on WO_2Cl_2 has also been noted by other workers,[4,7,23] and the disproportionation model is supported by tensimetric studies.[25,26]

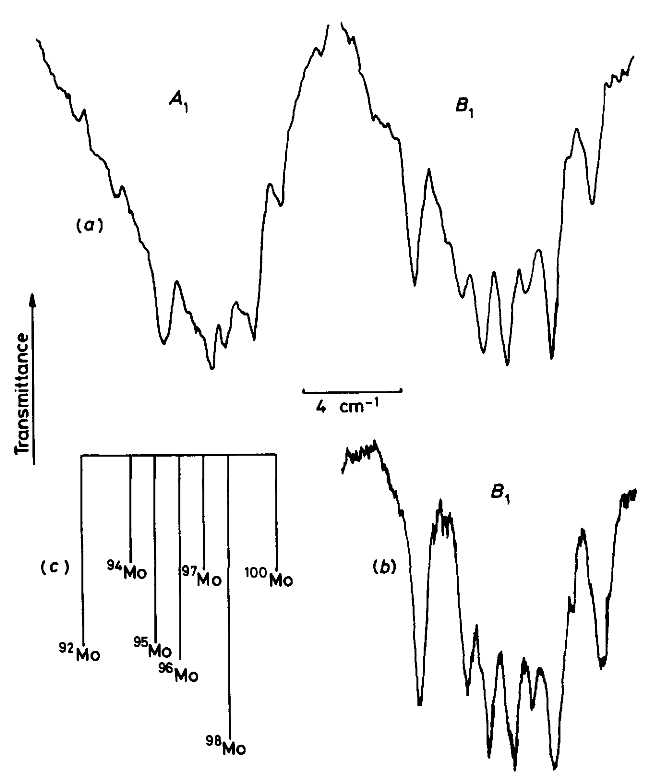

Figure 1. Isotope structure observed in the i.r. spectra of MoO_2X_2 molecules isolated in inert gas matrices at *ca.* 12 K: (*a*) ν_{A_1}(Mo=O) in MoO_2Cl_2 (Ar matrix 1 000—986 cm^{-1}) and ν_{B_1}(Mo=O) in MoO_2Cl_2 (Ar matrix 974—960 cm^{-1}); (*b*) ν_{B_1}(Mo=O) in MoO_2Br_2 (N_2 matrix 970—958 cm^{-1}); and (*c*) bar-graph showing relative abundances of molybdenum isotopes

Estimation of Bond Angles.—Figure 1(*a*) shows the high-resolution argon matrix spectrum of MoO_2Cl_2 in the M=O stretching region. Figure 1(*c*) shows the isotope abundances for naturally occurring molybdenum, and Figure 1(*b*) shows the antisymmetric (B_1) Mo=O stretch observed for MoO_2Br_2 in a nitrogen matrix. The fine structure on these bands is clearly due to molybdenum isotopes, and it is also evident that the components of the B_1 modes are moderately well resolved. If one considers this mode to be effectively uncoupled from the B_1 bending mode (assigned at <250 cm^{-1} for both MoO_2Cl_2 and MoO_2Br_2) the appropriate secular equation may be shown to be equation (1), where M_O and

$$\lambda_{B_1}(M{=}O) = (F_r - F_{rr})(1/M_O + 2\sin^2\theta/M_{Mo}) \quad (1)$$

M_{Mo} refer to the masses of oxygen and molybdenum, F_r and F_{rr} are the principal and interaction molybdenum–oxygen stretching force constants, and 2θ is the angle OMoO. If frequency data from two or more isotopic molybdenum species are available, this equation may in principle be used to estimate the interbond angle 2θ using the relationship (2),

$$\sin^2\theta = Mo'Mo''[(\omega')^2 - (\omega'')^2]/32[Mo''(\omega'')^2 - Mo'(\omega')^2] \quad (2)$$

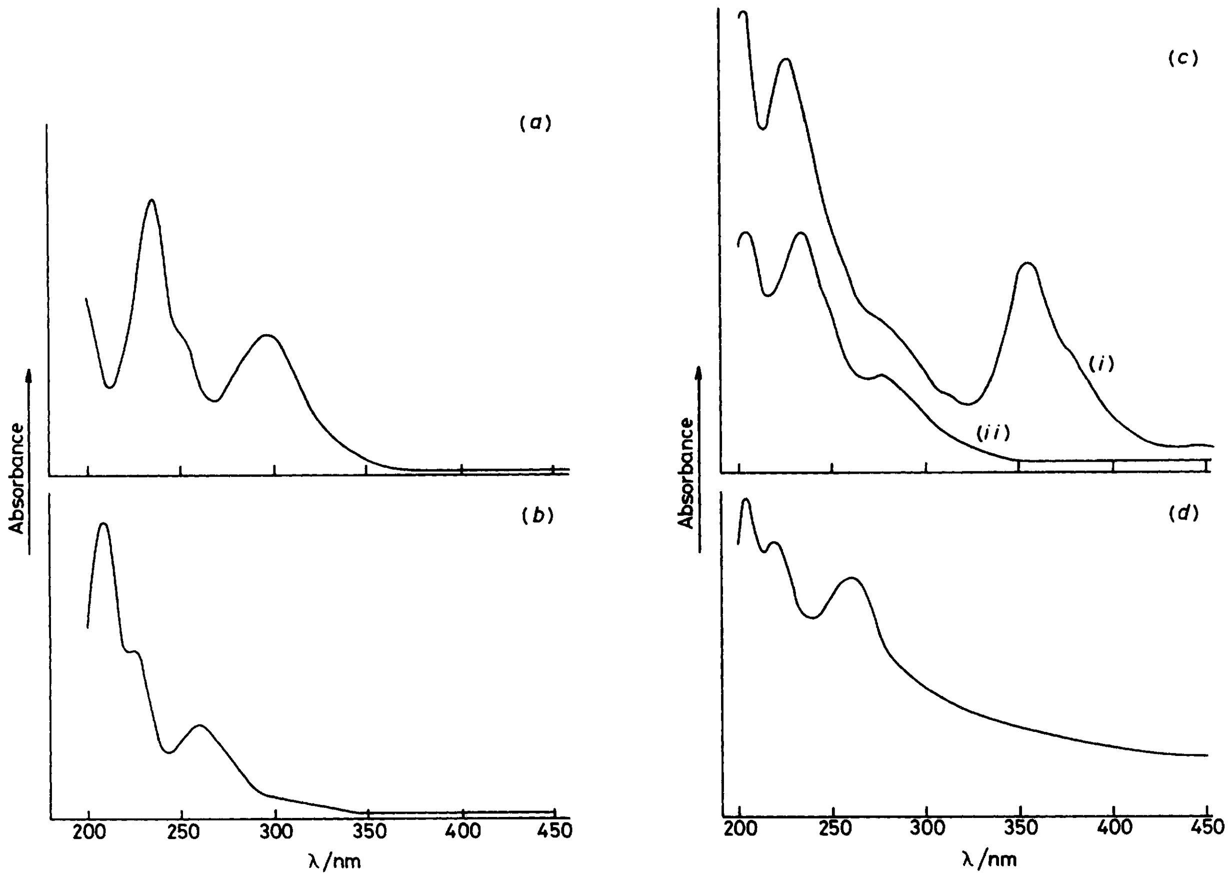

Figure 2. Electronic absorption spectra for MO_2X_2 species isolated in N_2 matrices at *ca.* 12 K: (*a*) MoO_2Br_2; (*b*) MoO_2Cl_2; (*c*) WO_2Cl_2, (*i*) containing $WOCl_4$, (*ii*) $WOCl_4$ subtracted; and (*d*) WO_2Br_2

where ω' and ω'' are the zero-order frequencies corresponding to molybdenum isotope masses Mo′ and Mo″. This expression assumes simple harmonic motion, but it has been shown that for CrO_2Cl_2 [27] and CrO_2F_2,[28] the use of observed vibrational transitions ν (uncorrected for anharmonicity) leads to estimates of OCrO angles from chromium isotope shifts which are in satisfactory agreement with other data. This approach has also been widely used to estimate bond angles in triatomic species.[29]

Application of this equation to the antisymmetric Mo=O stretching modes in MoO_2Cl_2 and MoO_2Br_2 leads to bond angles OMoO of 109 ± 3° for both species on the basis of the isotope data given in Table 1. The uncertainty quoted here essentially arises from the precision to which the ^{92}Mo–^{100}Mo shift could be measured ($\pm$0.2 cm^{-1}), but bearing in mind the approximations involved in the use of (1) and (2), it would be realistic to increase these error limits by a factor of two. Nevertheless, it is encouraging that our value for MoO_2Cl_2 is similar to the published electron diffraction value which gives OMoO = 104±2° for the gas-phase monomer.[8]

In the case of the tungsten analogues, we were unable to resolve a convincing W=O isotope pattern (the estimated peak separation is *ca.* 0.3 cm^{-1} per unit mass change of tungsten) but the intensity ratio of the W=O stretching modes provides an alternative route to the OWO angle (2θ). If these ($A_1 + B_1$) modes are separated from the remaining vibrational fundamentals, and the validity of the bond dipole model for i.r. intensities is assumed, it may readily be shown [30] that $I_{B_1}/I_{A_1} = \tan^2\theta(G_{B_1}/G_{A_1})$, where G_{B_1} and G_{A_1} are the appropriate *G*-matrix elements in the Wilson *G–F* approach. For the WO_2 unit in WO_2Cl_2 and WO_2Br_2, this equation reduces to (3),

$$I_{B_1}/I_{A_1} = \tan^2\theta(M_W + 32\sin^2\theta)/(M_W + 32\cos^2\theta) \quad (3)$$

where M_W is the atomic weight of tungsten.

Our estimates of the integrated i.r. absorptions of the W–O stretching modes give values for I_{B_1}/I_{A_1} of 1.91 ± 0.1 for both WO_2Cl_2 and WO_2Br_2, which imply bond angles of 107 ± 2° in both species. This approach has recently been applied to molecular K_2WO_4, which similarly shows two i.r. active W=O stretching modes in low-temperature matrices,[31] and the agreement with related electron diffraction data was satisfactory. It is difficult to assess the absolute accuracy of angles obtained using this approach, but the values obtained here for WO_2Cl_2 and WO_2Br_2 are very similar to those found for MoO_2Cl_2 and MoO_2Br_2 from isotope frequency shifts, and it might be anticipated that these four molecules would have comparable OMO bond angles in view of the close similarity between Mo^{VI} and W^{VI} compounds.

U.v.–Visible Studies.—Matrix isolation experiments to obtain the electronic spectra of these MO_2X_2 species generally employed nitrogen as the matrix gas, and somewhat lower vaporisation temperatures compared with the corresponding i.r. studies (see Experimental section). Typical results are shown in Figure 2. For MoO_2Cl_2, MoO_2Br_2, and WO_2Br_2, we are confident that these spectra are due to the monomeric species in view of our earlier i.r. results. However, with WO_2Cl_2, our spectra [see, for example, Figure 2(*c*)] show clear evidence of the additional presence of monomeric $WOCl_4$.

Table 2. Observed and calculated charge-transfer bands (cm^{-1}) for matrix-isolated MO_2X_2 species

Compound	Observed band [a]	Calc. I [b]	Calc. II [c]	Assignment
MoO_2Cl_2	44 440	45 000	45 000	c.t. O→Mo
	38 610	27 000	39 000	c.t. Cl→Mo
	32 680			
MoO_2Br_2	42 550	45 000	45 000	c.t. O→Mo
	39 680	21 000	33 000	c.t. Br→Mo
	33 780			
WO_2Cl_2	48 540	48 000	48 000	c.t. O→W
	42 730	30 000	42 000	c.t. Cl→W
	35 970			
WO_2Br_2	48 080	48 000	48 000	c.t. O→W
	38 610	24 000	36 000	c.t. Br→W

[a] Wavenumber positions obtained from spectra measured in wavelength. [b] Using $\chi_{\text{opt.}}$ values of 3.0 (Cl), 2.8 (Br), 3.6 (O), 2.1 (Mo), and 2.0 (W). [c] Using $\chi_{\text{opt.}}$ values of 3.0 (Cl), 2.8 (Br), 3.2 (O), 1.7 (Mo), and 1.6 (W).

The electronic spectrum of this molecule has previously been reported,[14] and its presence here was not entirely unexpected in view of the i.r. evidence. As a result, however, it was necessary to obtain the spectrum of WO_2Cl_2 by subtraction. Band maxima positions for all four MO_2X_2 species are given in Table 2.

Unlike CrO_2Cl_2, for which well resolved luminescence spectra have been obtained,[32] no emission was detected on exciting any of these MO_2X_2 species in any of their electronic absorption bands.

Interpretation. In principle, the assignment of electronic spectra can be attempted in several ways, and for this type of compound, the most popular methods involve either SCF–Xα–SW MO calculations,[10] the concept of optical electronegativity [33] [which gives the position of the lowest energy charge-transfer (c.t.) bands], or photoelectron spectroscopy. The observation of vibrational progressions serves to confirm band assignments, but unlike our previous study on MOX_4 systems,[14] such fine structure was not observed here.

A comparison between the He–I photoelectron spectra of CrO_2Cl_2 and MoO_2Cl_2 [12] reveals very similar energies for the six principal bands (A—F) * and this may be taken to indicate that the ordering of the occupied levels is the same for both molecules. We therefore assign the electronic transitions for MoO_2Cl_2 by analogy with CrO_2Cl_2,[10] and similar assignments for the remaining MO_2X_2 compounds would seem reasonable (Table 2).

Predictions of the lowest energy charge-transfer bands using optical electronegativities are generally satisfactory for $[MX_6]^{n-}$ ions,[33] and have given reasonable agreement with experiment for the five-co-ordinate species MOX_4 reported earlier.[14] For the above compounds, values of $\chi_{\text{opt.}}$ are taken to be Mo 2.1, W 2.0, O 3.6, Cl 3.0, and Br 2.8, and if these parameters are used directly to predict the positions of the c.t. bands in our MO_2X_2 species, the agreement for halogen→metal c.t. is poor (Table 2, Calc. I). However, Jorgensen [33] has argued that the strong π antibonding effect of oxide ligands in tetrahedrally co-ordinated complexes results in a lowering of the $\chi_{\text{opt.}}$ values for both metal and oxide. A second estimate of the positions of these bands may therefore be made taking $\chi_{\text{opt.}}(O^{2-})$ as 3.2 (ref. 33) and using data from $[MoO_4]^{2-}$ and $[WO_4]^{2-}$ to estimate χ values for Mo and W. These estimates (Table 2, Calc. II) give better overall agreement with our spectral data but still leave room for improvement. In particular, the prediction that the lowest energy X→M c.t. band in the bromides should lie below that in the chlorides is not borne out in practice, and the possibility remains that the long tails on the high-wavelength side of these bands contain unresolved c.t. maxima. Only a limited number of tetrahedral oxide halide molecules have been studied in this way, and a discussion of the assumptions involved in using $\chi_{\text{opt.}}$ data derived from $[MO_4]^{n-}$ species must be reserved until data are available on a wider range of compounds.

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* Principal bands for CrO_2Cl_2: A = 11.85, 11.97 (sh); B = 12.78; C = 13.24; D = 13.84; E = 14.3; F = 14.8 eV. MoO_2Cl_2: A = 11.93 (sh), 12.13, 12.21 (sh); B = 12.6, 12.67 (sh); C = 13.0; D = 13.76; E = 14.47; F = 14.93 eV (1 eV ≈ 1.602×10^{-19} J).

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