Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Experimental Evidence for the Molecular Molybdenum Fluorides MoF to MoF_6: a matrix isolation and DFT investigation.

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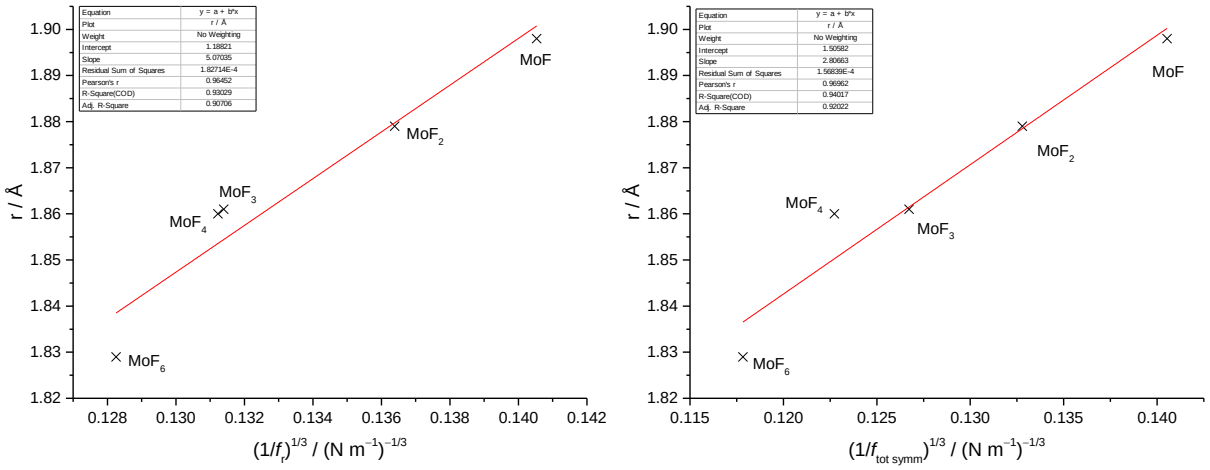

Figure ESI-1. Badger's rule (($r = (C/k)^{1/3} + d$)) plot of Mo-F bond length r vs $(1/k)^{1/3}$ for principal force constant f_r (left) and for the force constant derived from the totally symmetric mode $f_{tot\ symm}$ (right).

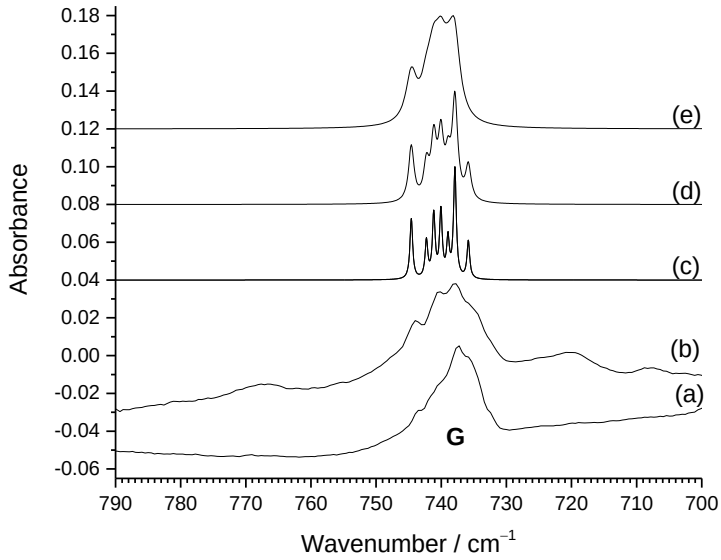

Figure ESI-2. Higher resolution (1.0 cm^{-1}) FTIR spectra of reaction products of atomic Mo in 1% F_2/Ar matrix with (a) the heated filament protected from F_2 using the Cu disc after deposition and annealing to 15 K, 20 and 25 K; and (b) without Cu disc after deposition; calculated (B3LYP/def2tzvpp) and scaled spectra for MoF_6 at (c) 0.5 cm^{-1}, (d) 1 cm^{-1} and 2 cm^{-1} fwhm.

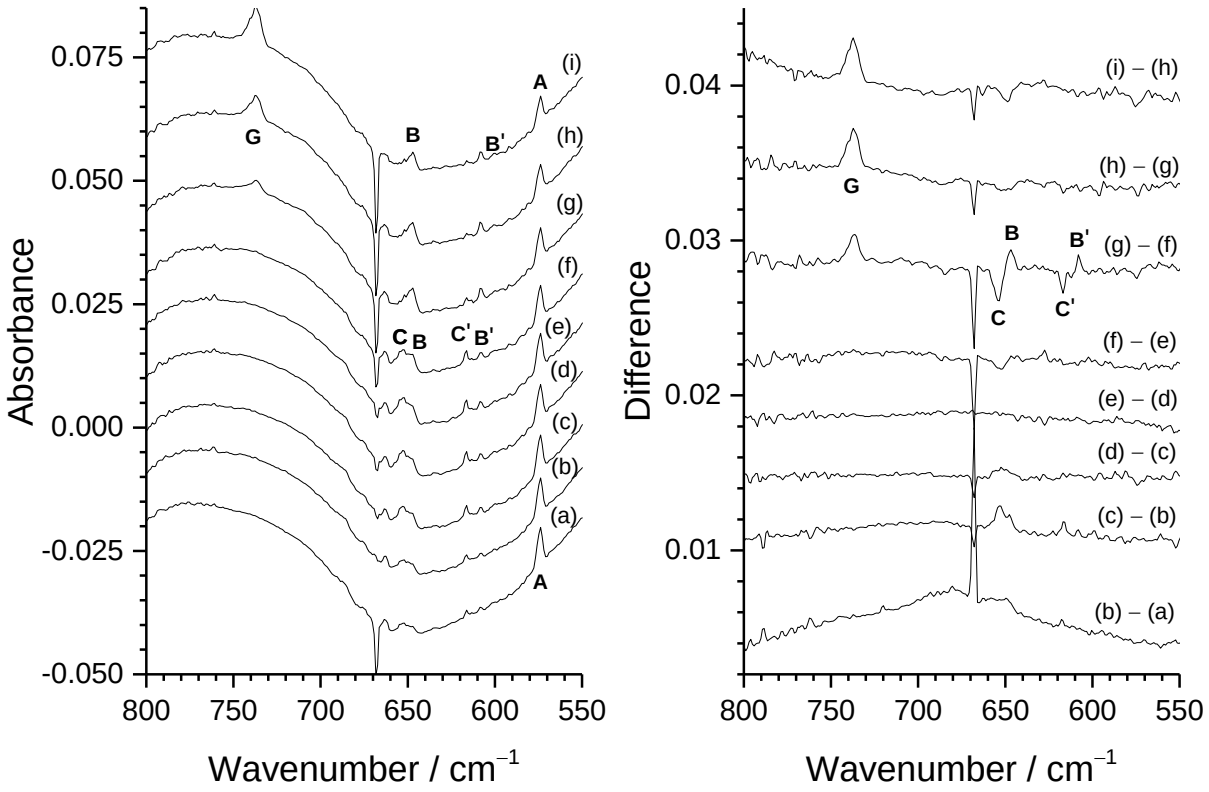

Figure ESI-3. FTIR spectra of reaction products of atomic Mo in 0.2% F_2/Ar matrix (a) after deposition; (b) after 10 mins visible light photolysis; (c) after 10 mins 200−410 nm photolysis; (d) after 10 mins broadband photolysis; (e) after further 10 mins visible light photolysis; (f) after 5 mins annealing at 15 K; (g) after 5 mins annealing at 20 K; (h) after 5 mins annealing at 25 K; (i) after 5 mins annealing at 30 K.

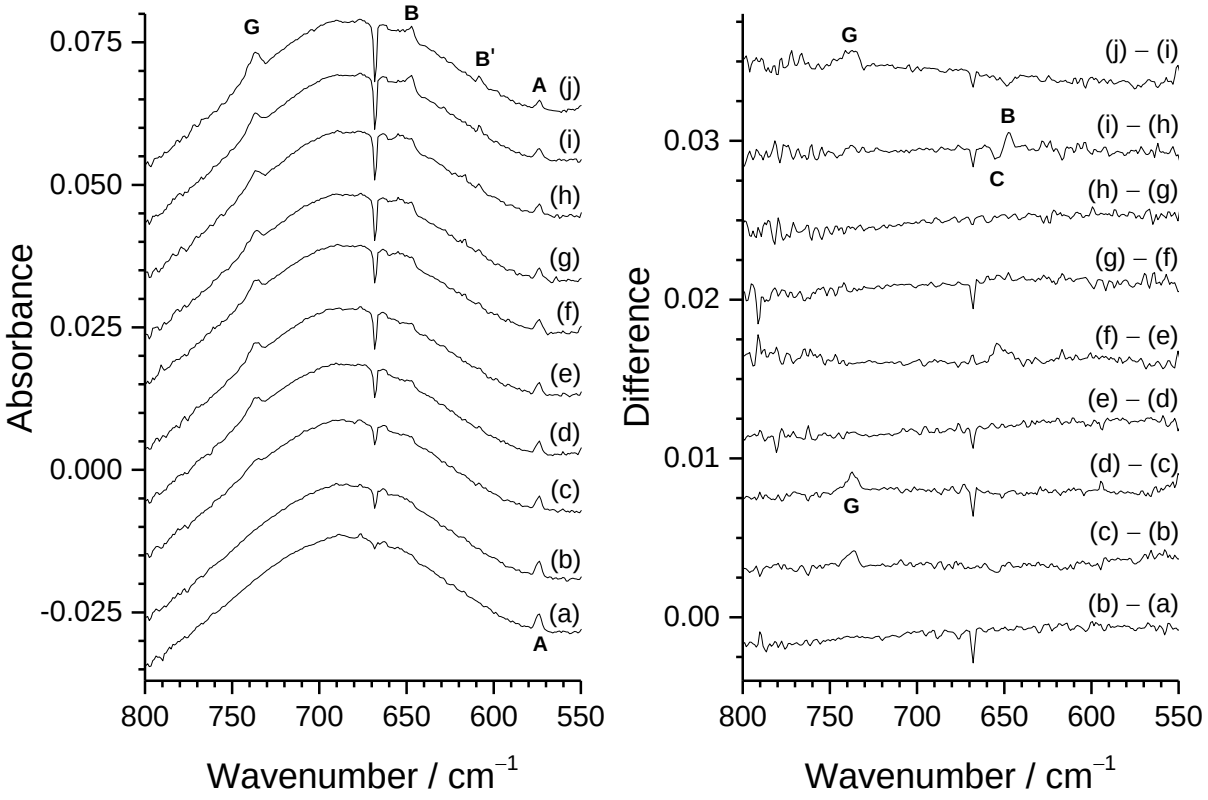

Figure ESI-4. FTIR absorbance and difference spectra of reaction products of atomic Mo in 0.2% F_2/Ar matrix (a) after deposition; (b) after 5 mins annealing at 15 K; (c) after 5 mins annealing at 20 K; (d) after 5 mins annealing at 25 K; (e) after 10 mins visible light photolysis; (f) after 10 mins 200−410 nm photolysis; (g) after 10 mins broadband photolysis; (h) after further 10 mins visible light photolysis; (i) after 5 mins annealing at 25 K; (j) after 5 mins annealing at 30 K.

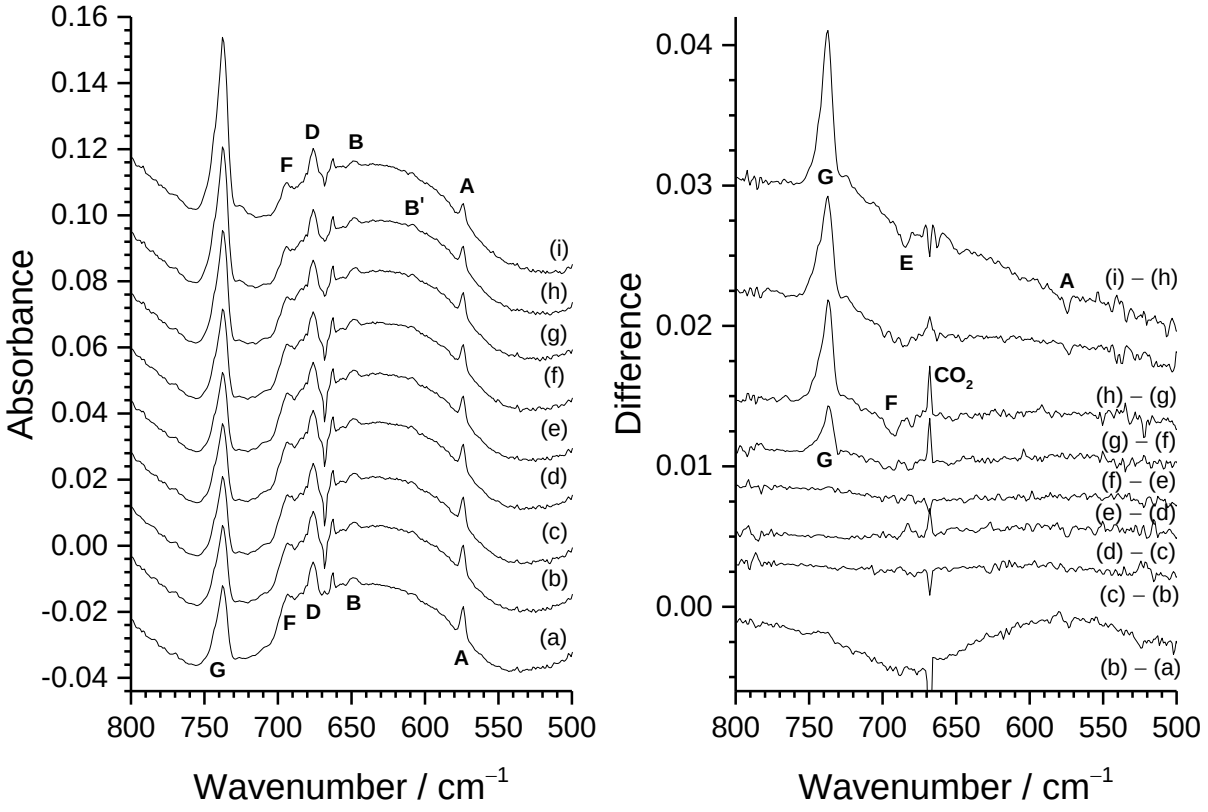

Figure ESI-5. FTIR absorbance and difference spectra of reaction products of atomic Mo in 2% F_2/Ar matrix (a) after deposition; (b) after 10 mins visible light photolysis; (c) after 10 mins 200−410 nm photolysis; (d) after 10 mins broadband photolysis; (e) after further 10 mins visible light photolysis; (f) after 5 mins annealing at 15 K; (g) after 5 mins annealing at 20 K; (h) after 5 mins annealing at 25 K; (i) after 5 mins annealing at 30 K.

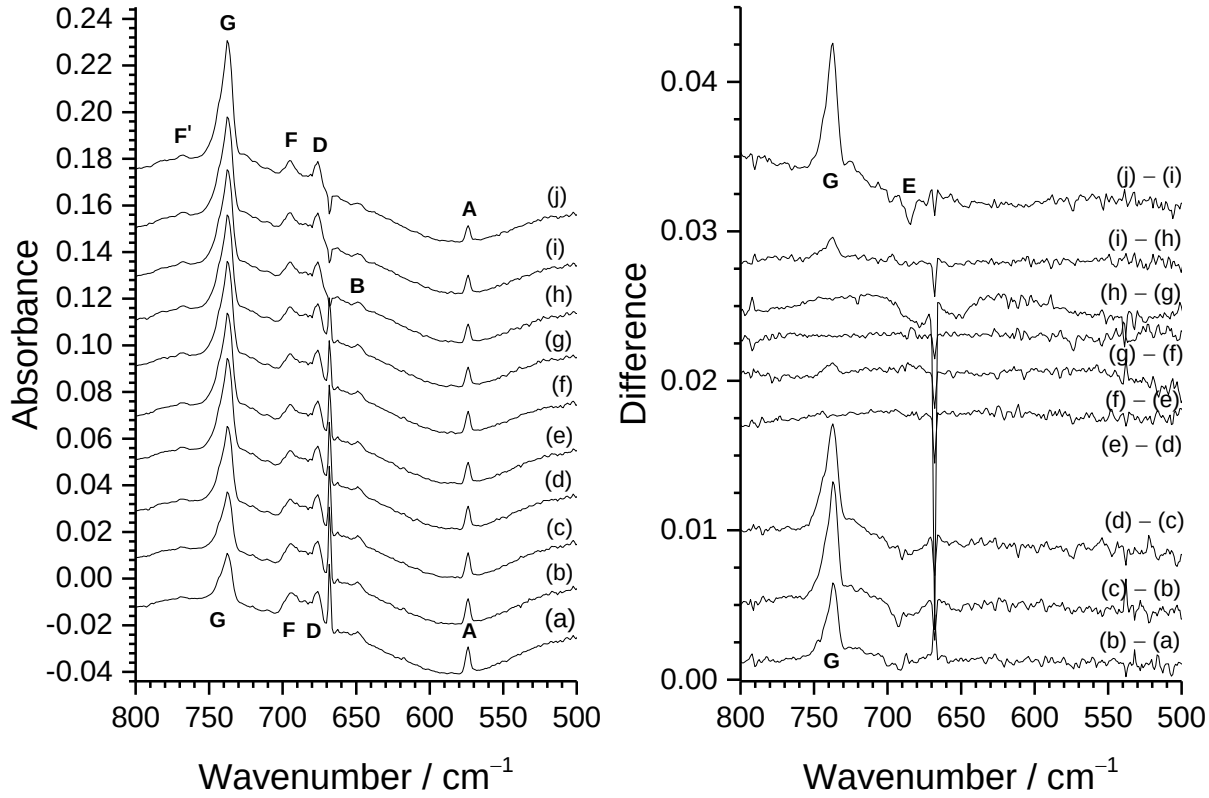

Figure ESI-6. FTIR absorbance and difference spectra of reaction products of atomic Mo in 2% F_2/Ar matrix (a) after deposition; (b) after 5 mins annealing at 15 K; (c) after 5 mins annealing at 20 K; (d) after 5 mins annealing at 25 K; (e) after 10 mins visible light photolysis; (f) after 10 mins 200−410 nm photolysis; (g) after 10 mins broadband photolysis; (h) after further 10 mins visible light photolysis; (i) after 5 mins annealing at 25 K; (j) after 5 mins annealing at 30 K.

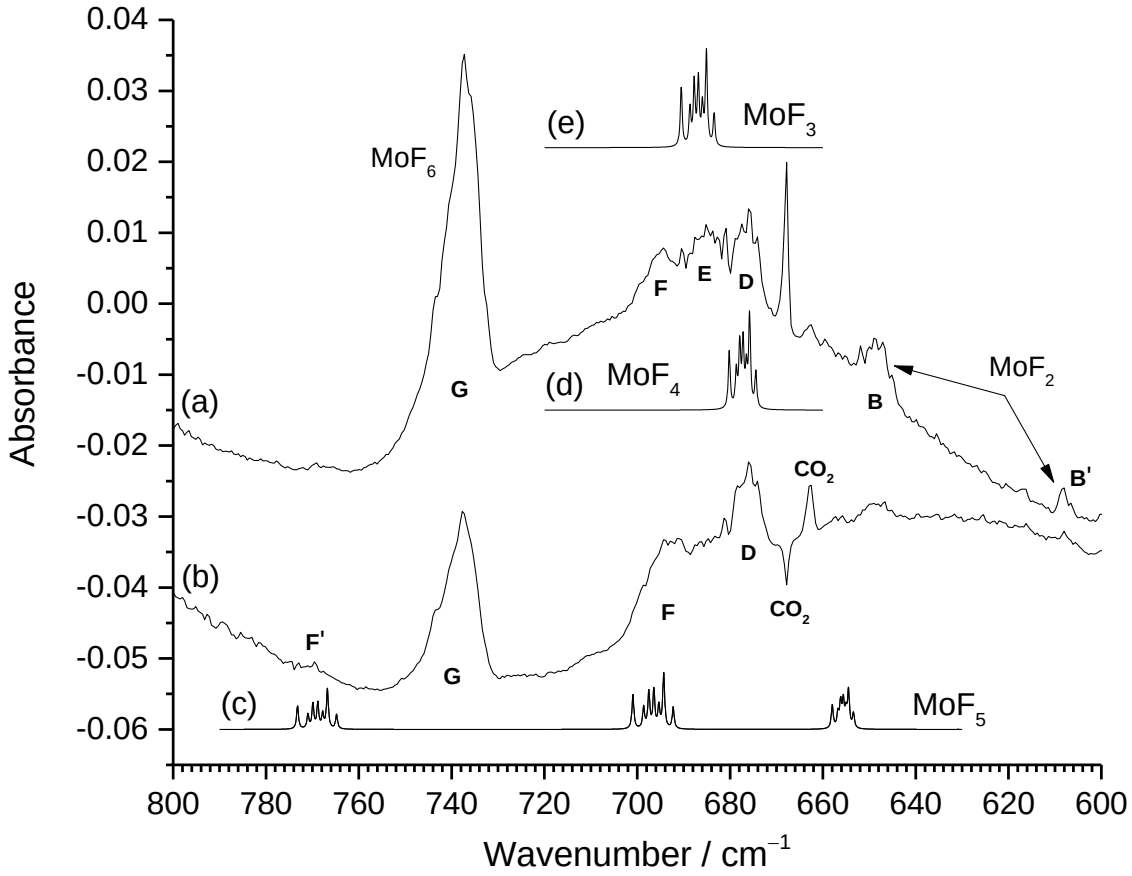

Figure ESI-7. Higher resolution (1.0 cm^{-1}) FTIR spectra of reaction products of atomic Mo (heated filament protected from F_2 using the Cu disc) in (a) 1% F_2/Ar matrix after deposition, broadband photolysis and annealing to 15 K, 20 and 25 K,;(b) in 2% F_2/Ar matrix; and calculated (B3LYP/def2tzvpp) and scaled spectra for (c) MoF_5; (d) MoF_4; and (e) MoF_3 at 0.5 cm^{-1} fwhm. Experimental features due to MoF_6 and MoF_2 are marked.

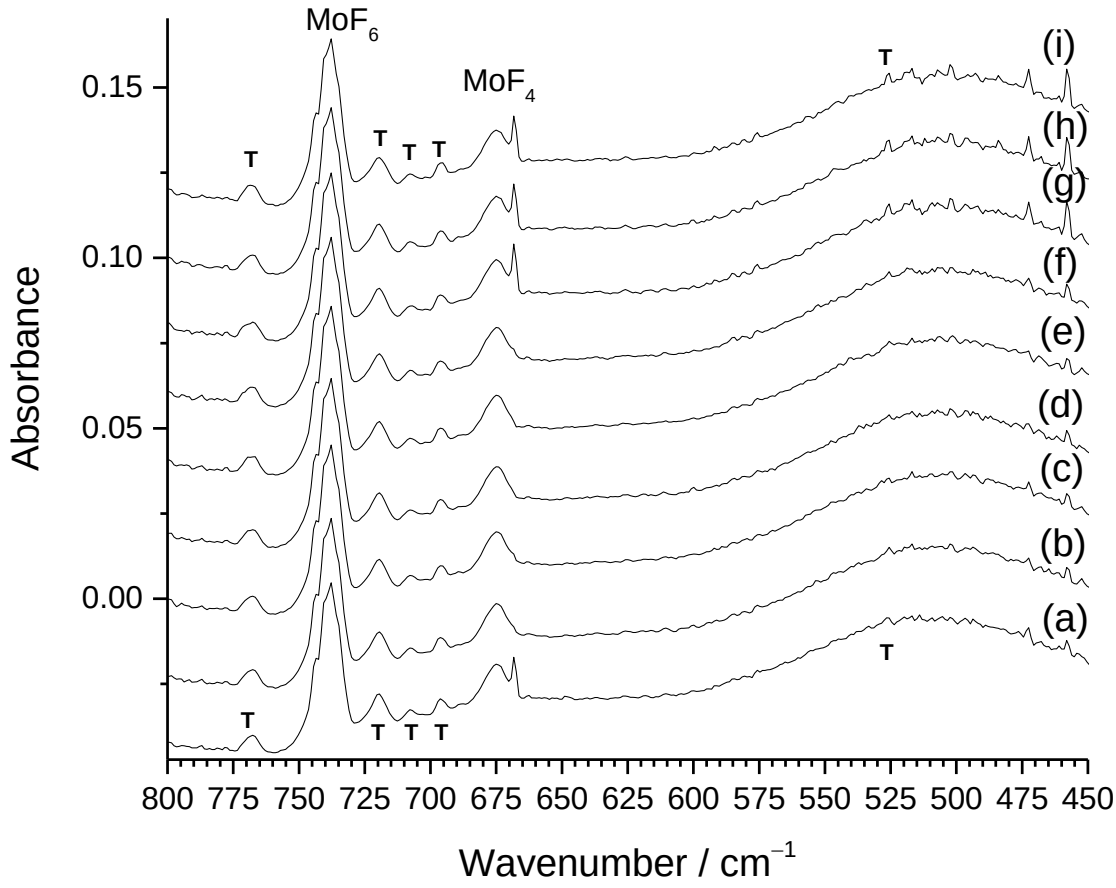

Figure ESI-8. FTIR spectra of reaction products of atomic Mo in 0.5% F_2/Ar matrix with the heated filament not protected from F_2 exposure: (a) after deposition; (b) after 10 mins visible light photolysis; (c) after 10 mins 200−410 nm photolysis; (d) after 10 mins broadband photolysis; (e) after further 10 mins visible light photolysis; (f) after 5 mins annealing at 15 K; (g) after 5 mins annealing at 20 K; (h) after 5 mins annealing at 25 K; (i) after 5 mins annealing at 30 K.

Table ESI-1. Calculated (B3LYP/def2tzvpp) geometries, vibrational modes and SVFF force constants of molybdenum fluoride molecules.

Assignments	Molecular structure	Electronic ground state	Mo–F Bond length /Å	F–Mo–F Bond angles	Vibrational modes cm^{-1} (IR intensity /km $mole^{-1}$)	Force constants N m^{-1}
MoF_6	Octahedral (O_h)	$^1A_{1g}$	1.829	90°	A_{1g} 739.0 (0.00) T_{1u} 734.2 (339 x 3) E_g 644.2 (0.00 x 2) T_{2g} 307.6 (0.00 x 3) T_{1u} 256.5 (33.2 x 3) T_{2u} 118.7 (0.00 x 3)	f_r = 474.0 f_{rr} = 24.46 f_{rr}' = 39.38
MoF_5	Distorted trigonal bipyramidal (C_1)	^2A	1.801 (eq) 1.819 (eq) 1.822 (eq) 1.876 (ax) 1.876 (ax)	110.5° (eq) 125.8° (eq) 123.7° (eq) 179.4° (ax) 90.0° 90.2° 89.7° 90.0° 90.2° 89.7°	761.5 (244) (eq str) 726.8 (0.004) (sym str breathing mode) 689.5 (355) (axial asymmetric str) 650.0 (228) (eq str) 626.5 (0.066) (asym str breathing mode) 278.1 (7.89) 236.3 (8.58) 217.1 (18.9) 211.2 (0.40) 193.3 (28.9) 90.1 (8.61) 31.7 (32.1)	
MoF_4	Tetrahedral (T_d)	$^3A_2$	1.860	109.47°	A_1 695.2 (0.00) T_2 678.8 (186 x 3) E 138.5 (0.00 x 2) T_2 124.9 (32.3 x 3)	f_r = 442.5 f_{rr} = 32.81
MoF_3	Trigonal planar (D_{3h})	$^4A_2'$	1.861	120°	E′ 692.3 (198 x 2) A_1' 662.6 (0.000) E′ 176.8 (7.11 x 2) A_2'' 142.1 (16.6)	f_r = 440.8 f_{rr} = 25.30
MoF_2	Bent (C_{2v})	$^5B_2$	1.879	132°	B_2 665.5 (198) A_1 635.0 (59.5) A_1 151.6 (8.84)	f_r = 394.2 f_{rr} = 32.89
MoF	($C_{\infty v}$)	$^6\Sigma^+$	1.898		Σ^+ 620.1 (148)	f_r = 360.3

Table ESI-2. Calculated (B3LYP/def2tzvpp) vibrational modes and SVFF *F* and *G* matrix elements and principal force constants (f_r) and interaction force constants (f_{rr} and f_{rr}') derived from them.

	mode	B3LYP def2tzvpp $\nu_{Mo\text{-}F}$ cm^{-1}	*G* matrix elements*	*G* g^{-1}	*F* N m^{-1}	*F* matrix elements	f_r N m^{-1}	f_{rr} N m^{-1}	f_{rr}' N m^{-1}
MoF	Σ^+	620.0	$\mu_F + \mu_{Mo}$	0.062850	360.3	f_r	360.3		
MoF_2	A_1	635.0	$\mu_F + \mu_{Mo}(1 + \cos\alpha)$	0.055628	427.1	$f_r + f_{rr}$	394.2	32.89	
	B_2	655.5	$\mu_F + \mu_{Mo}(1 - \cos\alpha)$	0.070072	361.3	$f_r - f_{rr}$	394.2	32.89	
MoF_3	A_1'	662.6	μ_F	0.052636	491.4	$f_r + 2f_{rr}$	440.8	25.30	
	E'	692.3	$\mu_F + (^3/_2)\mu_{Mo}$	0.067957	415.5	$f_r - f_{rr}$	440.8	25.30	
MoF_4	A_1	695.2	μ_F	0.052636	541.0	$f_r + 3f_{rr}$	442.5	32.81	
	T_2	678.8	$\mu_F + (^4/_3)\mu_{Mo}$	0.066255	409.7	$f_r - f_{rr}$	442.5	32.81	
MoF_6	A_{1g}	739.0	μ_F	0.052636	611.3	$f_r + 4f_{rr} + f_{rr}'$	474.0	24.46	39.38
	E_g	644.2	μ_F	0.052636	464.5	$f_r - 2f_{rr} + f_{rr}'$	474.0	24.46	39.38
	T_{1u}	734.2	$\mu_F + 2\mu_{Mo}$	0.073064	434.7	$f_r - f_{rr}'$	474.0	24.46	39.38

* μ_F and μ_{Mo} are the reciprocal masses of ^{19}F and ^{98}Mo. $F = ((\nu/130.283)^2/G)$. f_r is the principal force constant and f_{rr} the interaction force constant. For MoF_6, f_{rr} is the interaction force constant for the stretching modes *cis* to each other, and f_{rr}' for those trans to each other. (K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds: Part A: Theory and Applications in Inorganic Chemistry, Sixth Edition*, John Wiley & Sons, Inc., 2008.)

Table ESI-3. Comparison of MoF_6 force constants

f_r	f_{rr}	f_{rr}'	Ref
474.0	24.5	39.4	(a)
508.0	24.6	4.0	(b)
473	24.4	35	(c)
494	23	29	(d)
508.3	25.33	5.0	(e)

(a) this work
(b) C. W. F. T. Pistorius, *J. Chem. Phys.*, 1958, **29**, 1328-1332.
(c) H. H. Claassen, *J. Chem. Phys.*, 1959, **30**, 968-972.
(d) R. S. McDowell, R. J. Sherman, L. B. Asprey and R. C. Kennedy, *J. Chem. Phys.*, 1975, **62**, 3974-3978.
(e) F. Ucun and M. G. Şengül, *Z. Naturforsch., A: Phys. Sci.*, 2005, **60**, 819-822.

Table ESI-4. Cartesian coordinates and energies of minimised structures at the B3LYP/def2tzvpp. (No negative frequencies were reported for these structures)

MoF $^{6}\Sigma^{+}$

Centre Number	Atomic Number	Atomic Type	Coordinates (Å)		
			X	Y	Z
1	42	0	0.000000	0.000000	0.334978
2	9	0	0.000000	0.000000	−1.563229

E(UB3LYP) = −168.075224090 h
Zero-point correction= 0.001413 (Hartree/Particle)
Thermal correction to Energy= 0.003922
Thermal correction to Enthalpy= 0.004867
Thermal correction to Gibbs Free Energy= -0.023251
Sum of electronic and zero-point Energies= -168.073811
Sum of electronic and thermal Energies= -168.071302
Sum of electronic and thermal Enthalpies= -168.070357
Sum of electronic and thermal Free Energies= -168.098476

MoF_2 $^{5}B_2$

Centre Number	Atomic Number	Atomic Type	Coordinates (Å)		
			X	Y	Z
1	42	0	0.000000	0.000000	0.229137
2	9	0	0.000000	−1.716548	−0.534652
3	9	0	0.000000	1.716548	−0.534652

E(UB3LYP) = −268.043295656 h
Zero-point correction= 0.003308 (Hartree/Particle)
Thermal correction to Energy= 0.007050
Thermal correction to Enthalpy= 0.007994
Thermal correction to Gibbs Free Energy= -0.025125
Sum of electronic and zero-point Energies= -268.039988
Sum of electronic and thermal Energies= -268.036245
Sum of electronic and thermal Enthalpies= -268.035301
Sum of electronic and thermal Free Energies= -268.068421

MoF_3 $^4A_2$'

Centre Number	Atomic Number	Atomic Type	Coordinates (Å)		
			X	Y	Z
1	42	0	0.000000	0.000000	0.000000
2	9	0	0.000000	1.861323	0.000000
3	9	0	−1.611953	−0.930661	0.000000
4	9	0	1.611953	−0.930661	0.000000

E(UB3LYP) = −368.016658598 h
Zero-point correction= 0.005793 (Hartree/Particle)
Thermal correction to Energy= 0.010839
Thermal correction to Enthalpy= 0.011783
Thermal correction to Gibbs Free Energy= -0.023698
Sum of electronic and zero-point Energies= -368.010866
Sum of electronic and thermal Energies= -368.005820
Sum of electronic and thermal Enthalpies= -368.004876
Sum of electronic and thermal Free Energies= -368.040357

MoF_4 $^3A_2$

Centre Number	Atomic Number	Atomic Type	Coordinates (Å)		
			X	Y	Z
1	42	0	0.000000	0.000000	0.000000
2	9	0	1.074031	1.074031	1.074031
3	9	0	−1.074031	−1.074031	1.074031
4	9	0	−1.074031	1.074031	−1.074031
5	9	0	1.074031	−1.074031	−1.074031

E(UB3LYP) = −467.956986927 h
Zero-point correction= 0.007708 (Hartree/Particle)
Thermal correction to Energy= 0.014410
Thermal correction to Enthalpy= 0.015355
Thermal correction to Gibbs Free Energy= -0.023433
Sum of electronic and zero-point Energies= -467.949279
Sum of electronic and thermal Energies= -467.942576
Sum of electronic and thermal Enthalpies= -467.941632
Sum of electronic and thermal Free Energies= -467.980419

MoF_5 ^2A

Centre Number	Atomic Number	Atomic Type	Coordinates (Å)		
			X	Y	Z
1	42	0	0.000050	−0.029727	0.006652
2	9	0	−0.000667	0.916429	−1.550663
3	9	0	−1.876054	−0.023321	0.000535
4	9	0	−0.000732	1.096769	1.435371
5	9	0	1.876194	−0.021563	0.000498
6	9	0	0.001024	−1.829588	0.083217

E(UB3LYP) = −567.878041967 h
Zero-point correction= 0.010735 (Hartree/Particle)
Thermal correction to Energy= 0.018388
Thermal correction to Enthalpy= 0.019333
Thermal correction to Gibbs Free Energy= -0.024005
Sum of electronic and zero-point Energies= -567.867307
Sum of electronic and thermal Energies= -567.859653
Sum of electronic and thermal Enthalpies= -567.858709
Sum of electronic and thermal Free Energies= -567.902047

MoF_6 $^1A_{1g}$

Centre Number	Atomic Number	Atomic Type	Coordinates (Å)		
			X	Y	Z
1	42	0	0.000000	0.000000	0.000000
2	9	0	0.000000	0.000000	1.829184
3	9	0	0.000000	1.829184	0.000000
4	9	0	−1.829184	0.000000	0.000000
5	9	0	0.000000	0.000000	−1.829184
6	9	0	0.000000	−1.829184	0.000000
7	9	0	1.829184	0.000000	0.000000

E(RB3LYP) = −667.789350335 h
Zero-point correction= 0.014303 (Hartree/Particle)
Thermal correction to Energy= 0.022570
Thermal correction to Enthalpy= 0.023514
Thermal correction to Gibbs Free Energy= -0.016453
Sum of electronic and zero-point Energies= -667.775047
Sum of electronic and thermal Energies= -667.766781
Sum of electronic and thermal Enthalpies= -667.765837
Sum of electronic and thermal Free Energies= -667.805804

Mo $^{7}S_{3}$

E(UB3LYP) = -68.1232861644

Zero-point correction= 0.000000 (Hartree/Particle)

Thermal correction to Energy= 0.001416

Thermal correction to Enthalpy= 0.002360

Thermal correction to Gibbs Free Energy= -0.018318

Sum of electronic and zero-point Energies= -68.123286

Sum of electronic and thermal Energies= -68.121870

Sum of electronic and thermal Enthalpies= -68.120926

Sum of electronic and thermal Free Energies= -68.141604

F_2 $^{1}\Sigma_g^{+}$

Centre Number	Atomic Number	Atomic Type	Coordinates (Å)		
			X	Y	Z
1	9	0	3.446093	1.125828	0.000000
2	9	0	2.049536	1.125828	0.000000

E(RB3LYP) = -199.599540492 h

Zero-point correction= 0.002387 (Hartree/Particle)

Thermal correction to Energy= 0.004778

Thermal correction to Enthalpy= 0.005722

Thermal correction to Gibbs Free Energy= -0.017231

Sum of electronic and zero-point Energies= -199.597154

Sum of electronic and thermal Energies= -199.594763

Sum of electronic and thermal Enthalpies= -199.593819

Sum of electronic and thermal Free Energies= -199.616771

Ar $^{1}S_{0}$

E(RB3LYP) = -527.549964127 h

Zero-point correction= 0.000000 (Hartree/Particle)

Thermal correction to Energy= 0.001416

Thermal correction to Enthalpy= 0.002360

Thermal correction to Gibbs Free Energy= -0.015212

Sum of electronic and zero-point Energies= -527.549964

Sum of electronic and thermal Energies= -527.548548

Sum of electronic and thermal Enthalpies= -527.547604

Sum of electronic and thermal Free Energies= -527.565176

ArMoF (linear) $^6\Sigma^+$

Centre Number	Atomic Number	Atomic Type	Coordinates (Å)		
			X	Y	Z
1	42	0	0.000000	0.000000	0.487129
2	9	0	0.000000	0.000000	2.399874
3	18	0	0.000000	0.000000	-2.336572

E(UB3LYP) = -695.629297831 h
Zero-point correction= 0.001758 (Hartree/Particle)
Thermal correction to Energy= 0.006744
Thermal correction to Enthalpy= 0.007688
Thermal correction to Gibbs Free Energy= -0.029398
Sum of electronic and zero-point Energies= -695.627539
Sum of electronic and thermal Energies= -695.622554
Sum of electronic and thermal Enthalpies= -695.621610
Sum of electronic and thermal Free Energies= -695.658695

	Π	Π	Σ^+	Σ^+
Frequencies /cm^{-1}	36.6160	36.6160	97.8595	600.7694
IR Intensity / km mole^{-1}	2.7210	2.7210	2.0407	158.5581

ArMoF (bent) $^6A'$

Centre Number	Atomic Number	Atomic Type	Coordinates (Å)		
			X	Y	Z
1	42	0	0.000000	0.488575	0.000000
2	9	0	0.140952	2.395452	0.000000
3	18	0	-0.070476	-2.337735	0.000000

E(UB3LYP) = -695.629388039 h
Zero-point correction= 0.001799 (Hartree/Particle)
Thermal correction to Energy= 0.006287
Thermal correction to Enthalpy= 0.007231
Thermal correction to Gibbs Free Energy= -0.027537
Sum of electronic and zero-point Energies= -695.627589
Sum of electronic and thermal Energies= -695.623101
Sum of electronic and thermal Enthalpies= -695.622157
Sum of electronic and thermal Free Energies= -695.656925

	A′	A′	A′
Frequencies /cm^{-1}	87.3607	97.8393	604.3087
IR Intensity / km mole^{-1}	2.8508	1.9473	158.6219