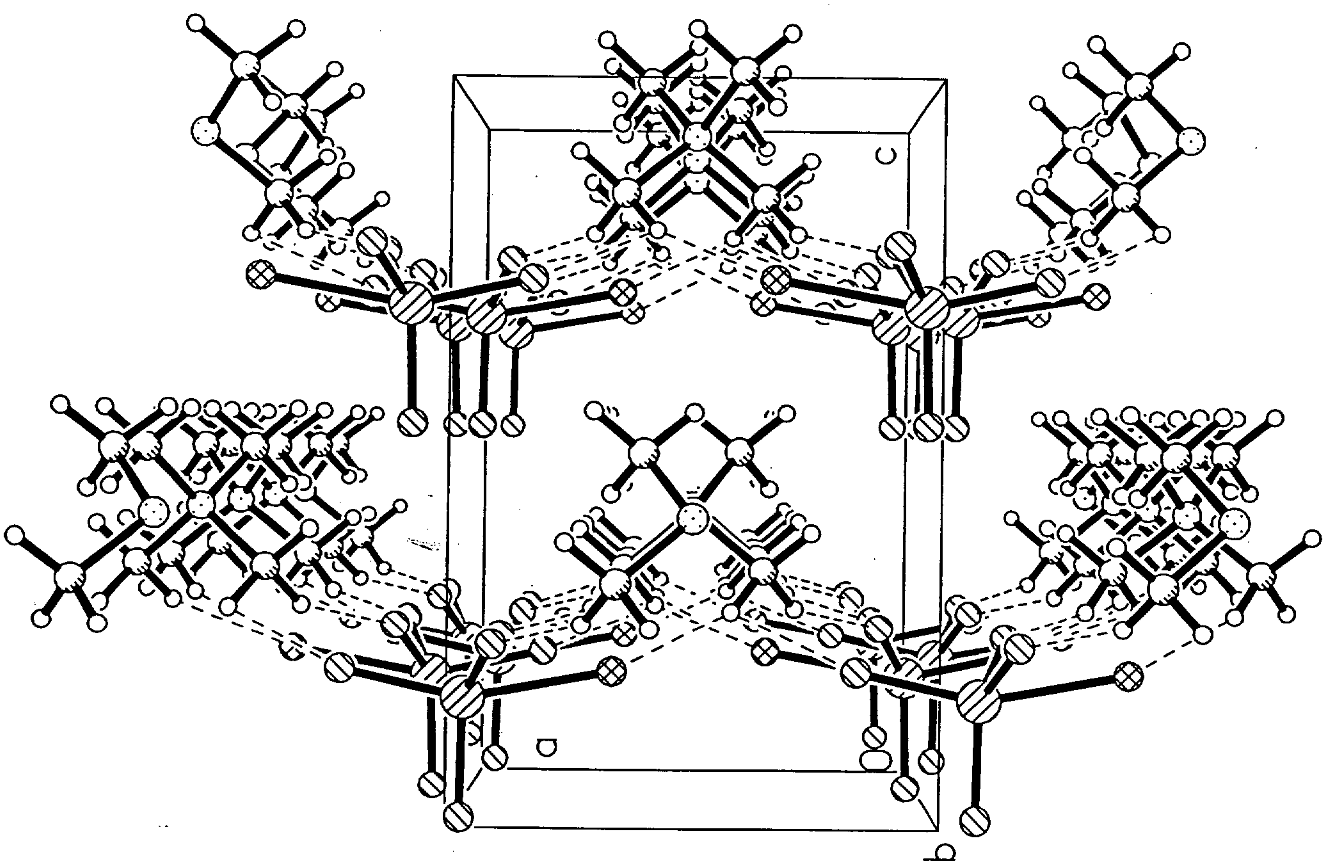


Figure S6. View of the $[N(CH_3)_4][OsO_4F]$ unit cell showing the packing along the *b*-axis.

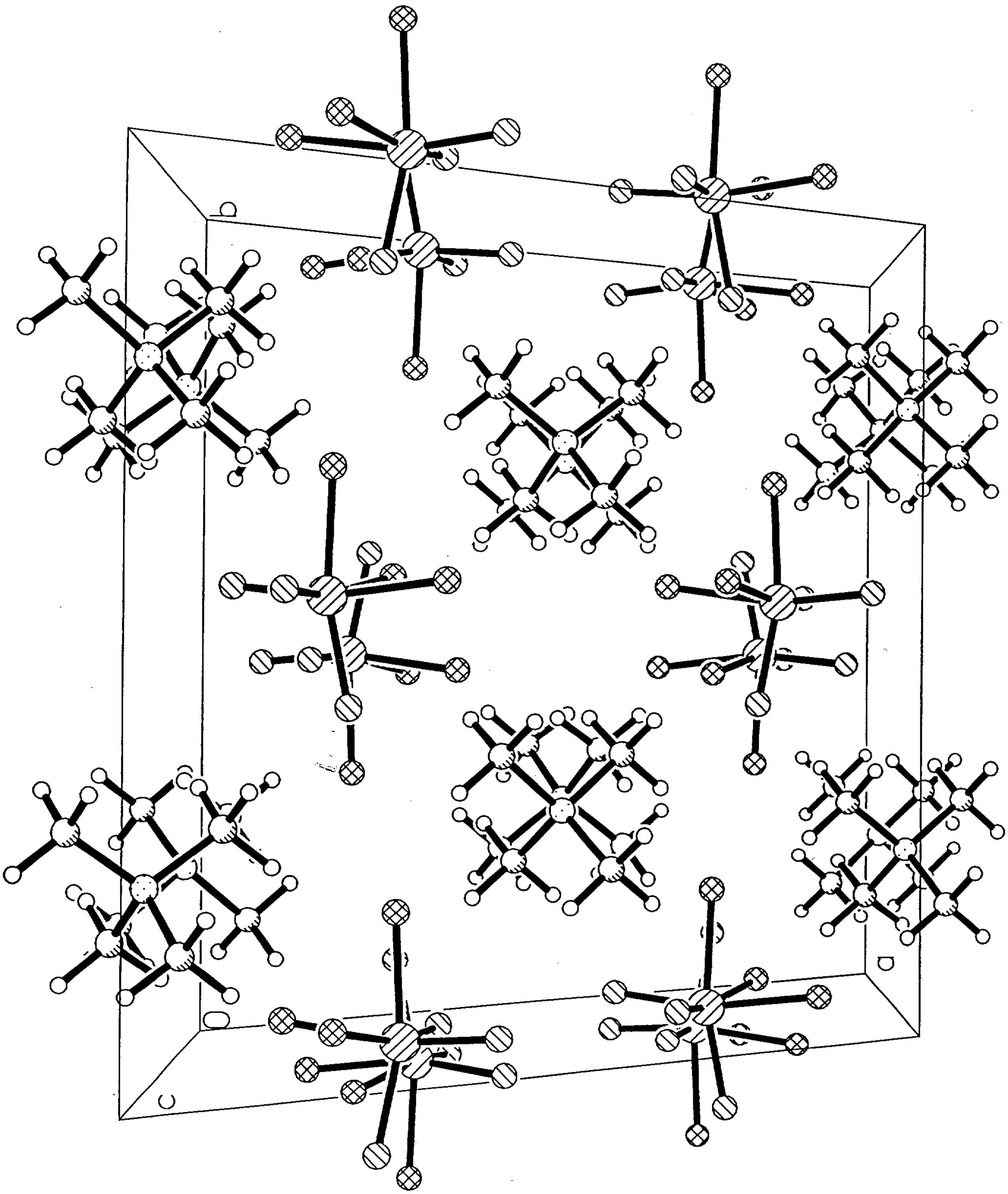


Figure S7. View of the $[N(CH_3)_4][OsO_3F_3]$ unit cell showing the packing along the *c*-axis.

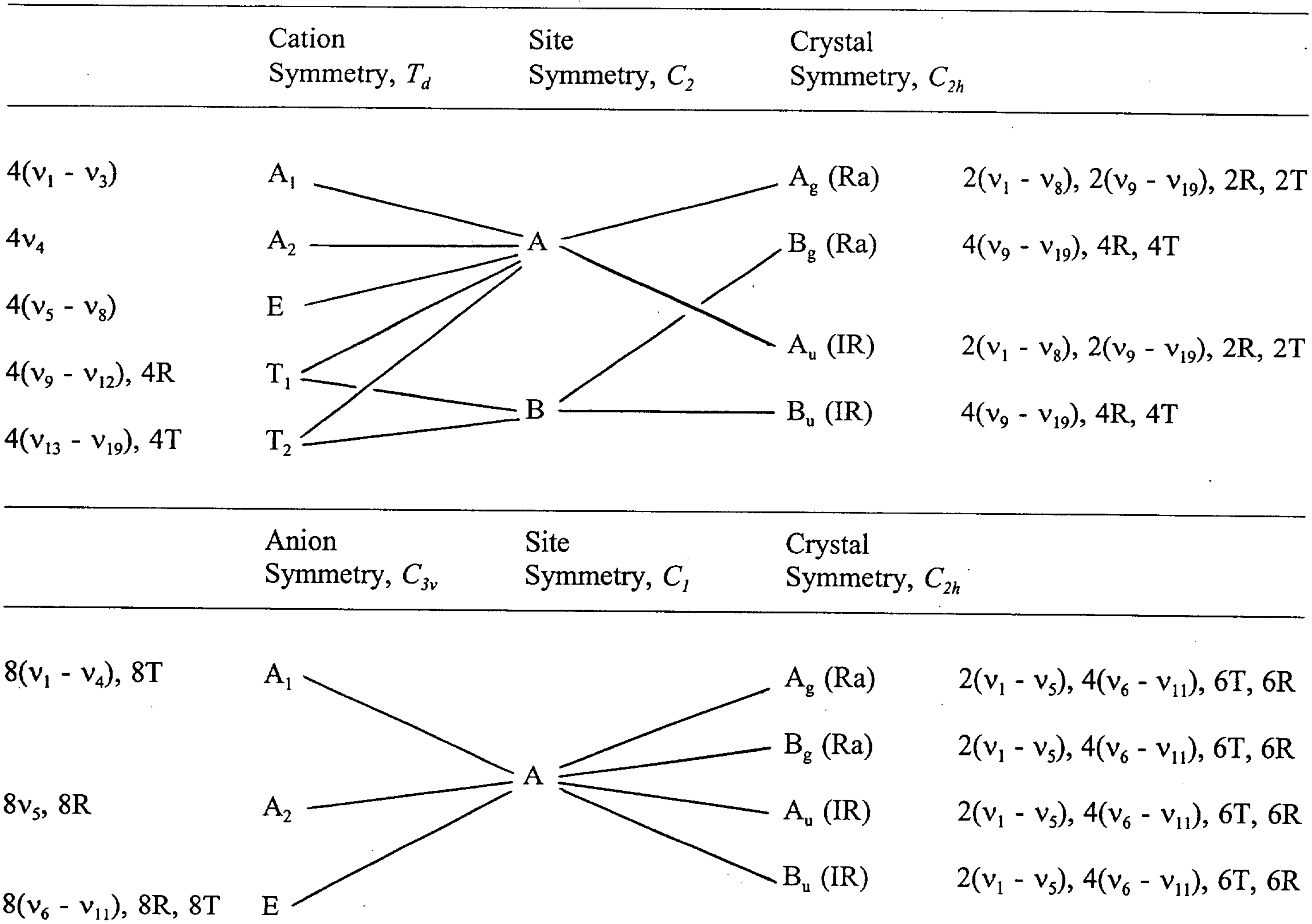
Table S8. Correlation Diagram for the Vibrational Modes of the a) $N(CH_3)_4^+$ Cation and b) OsO_4F^- Anion in $[N(CH_3)_4][OsO_4F]$.[a]

	Cation Symmetry, T_d	Site Symmetry, C_2	Crystal Symmetry, C_{2v}	
$4(\nu_1 - \nu_3)$	A_1		A_1 (Ra, IR)	$2(\nu_1 - \nu_8)$, $2(\nu_9 - \nu_{19})$, 2R, 2T
$4\nu_4$	A_2	A		
			A_2 (Ra)	$2(\nu_1 - \nu_8)$, $2(\nu_9 - \nu_{19})$, 2R, 2T
$4(\nu_5 - \nu_8)$	E			
$4(\nu_9 - \nu_{12})$, 4R	T_1			
		B	B_1 (Ra, IR)	$4(\nu_9 - \nu_{19})$, 4R, 4T
$4(\nu_{13} - \nu_{19})$, 4T	T_2			
			B_2 (Ra, IR)	$4(\nu_9 - \nu_{19})$, 4R, 4T

	Anion Symmetry, C_s	Site Symmetry, C_s	Crystal Symmetry, C_{2v}	
$4(\nu_1 - \nu_8)$, 8T, 4R	A′	A′	A_1 (Ra, IR)	$2(\nu_1 - \nu_8)$, 4T, 2R
			A_2 (Ra, IR)	$2(\nu_9 - \nu_{12})$, 2T, 4R
$4(\nu_9 - \nu_{12})$, 4T, 8R	A″	A″	B_1 (Ra)	$2(\nu_1 - \nu_8)$, 4T, 2R
			B_2 (Ra)	$2(\nu_9 - \nu_{12})$, 2T, 4R

[a] Correlation of the free anion symmetry of OsO_4F^- (C_s) to the anion site symmetry (C_s) and the unit cell symmetry (C_{2v}) (space group *Abm2*) predicts that the A′ modes of the free anion are each split into A_1 and B_1 components in the Raman and infrared spectra. The A″ modes are expected to split into A_2 and B_2 components in the Raman spectrum while the splitting is not observed in the infrared spectrum. Correlation of the free cation symmetry of $N(CH_3)_4^+$ (T_d) to the cation site symmetry (C_2) and the unit cell symmetry (C_{2v}) predicts that all bands (ν_1 - ν_{19}) are Raman and infrared active. In the Raman spectrum, the bands ν_1 - ν_8 and ν_9 - ν_{19} are expected to be factor-group split into A_1 and A_2 and into A_1, A_2, B_1, and B_2 components, respectively. In the infrared spectrum, the bands ν_1 - ν_8 are not expected to be split while the bands ν_9 - ν_{19} are expected to split into A_1, B_1, and B_2 components.

Table S9. Correlation Diagram for the Vibrational Modes of the a) $N(CH_3)_4^+$ Cation and b) $OsO_3F_3^-$ Anion in $[N(CH_3)_4][OsO_3F_3]$.[a]



[a] Correlation of the free anion symmetry of $OsO_3F_3^-$ (C_{3v}) to the anion site symmetry (C_1) and the unit cell symmetry (C_{2h}) (space group *C2/c*) predicts that all the vibrational bands are Raman and infrared active and are split into A_g and B_g components and into A_u and B_u components in the Raman and infrared spectrum, respectively. Correlation of the free cation symmetry of $N(CH_3)_4^+$ (T_d) to the cation site symmetry (C_2) and the unit cell symmetry (C_{2h}) predicts that all bands are Raman and infrared active. In the Raman and infrared spectra ν_1 - ν_8 are not expected to show factor-group splitting, while ν_9 - ν_{19} are expected to be factor-group split into A_g and B_g components and into A_u and B_u components in the Raman and infrared spectrum, respectively.