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Molecular Structures of Arsenic Trifluoride and Arsenic Pentafluoride as Determined by Electron Diffraction[1]

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Arsenic trifluoride was found to have a bond length of $r_g = 1.706 \pm 0.002$ Å and an F–As–F angle of 96.2 ± 0.2°. The bond angle is the smallest so far reported in the series of arsenic trihalides. This finding is contrary to the most frequently cited structure trend and requires the modification of a subrule of the valence shell–electron pair repulsion theory. The pentafluoride molecule was found to be a trigonal bipyramid with axial bonds 0.055 ± 0.010 Å longer than equatorial bonds and an average r_g arsenic–fluorine bond length of 1.678 ± 0.002 Å; values for $r_g(\text{As–F}_{ax})$ and $r_g(\text{As–F}_{eq})$ were 1.711 ± 0.005 and 1.656 ± 0.004 Å, respectively. Uncertainties listed are estimated standard errors. Root-mean-square amplitudes of vibration were determined and are discussed in the text.

Introduction

Arsenic trifluoride was one of several molecules for which structures were reported in an early electron diffraction paper by Pauling and Brockway,[3] who, using the radial distribution function method, reported an As–F bond length of 1.70 ± 0.02 Å as the single AsF_3 parameter determined. Before these results were published, Yost and Sherborne,[4] of the same laboratory, estimated that the F–As–F angle was about 97° on the basis of their own Raman investigation of the molecule. In a 1934 discussion of the Raman spectra and vibrational frequencies of AB_3 trihalide molecules, Howard and Wilson[5] estimated a value of 1.80 Å for the As–F distance, assuming the bond angle of Yost and Sherborne. Nearly 20 years later, Dailey, *et al.*, and Kisliuk and Geschwind[6,7] reported the As–F distance as 1.712 ± 0.005 Å according to a microwave study and estimated the F–As–F angle from quadrupole interactions[8,9] by means of a comparison with $AsCl_3$ as being 102 ± 2°. After their work, the experimentally determined arsenic(III) halide bond angles commonly referred to were 102 ± 2, 98.7 ± 0.3,[10] 99.7 ± 0.3,[11] and 100.2 ± 0.4°[12] for the fluoride, chloride, bromide, and iodide, respectively. A similarly irregular trend was noted for the phosphorus(III) trihalides. These irregularities prompted the publication of a number of conjectures on the quantum theoretical implications.

The molecular spectra of AsF_5 and the pentafluorides of antimony and bromine were the subjects of a 1955 dissertation.[13] Hoskins and Lord[14] calculated the height of the barrier to internal exchange of fluorine nuclei in AsF_5 and in the analogous PF_5. O'Hare and Hubbard's[15] report that the average bond energy in arsenic trifluoride was about 20 kcal/mol greater than in arsenic pentafluoride suggested that a structural investigation of the relative bond lengths in AsF_3 and AsF_5 might be worthwhile. In the analogous phosphorus compounds, existing information, since found to be unreliable, made the bond length in PF_3 the same as the average in PF_5,[16] despite the fact that the bond energy in PF_3 is greater than in PF_5.[17]

It was therefore of interest to undertake structural investigations of the AsF_3 and AsF_5 molecules for two reasons: (A) to test the rather uncertain experimental evidence for assigning a value of 102° to the F–As–F angle in AsF_3, which would make it the largest in the X–As–X series, and (B) to make the comparison between bonds in AsF_3 and AsF_5 that had been made between PF_3 and PF_5.

Experimental Section

Samples of AsF_3 and AsF_5 were purchased from the Ozark-Mahoning Co., Tulsa, Okla., and were used without further purification. The AsF_3 was of stated purity greater than 99.9%; the other sample was more than 99% AsF_5, with the principal impurities listed as HF and AsF_3.

The electron diffraction apparatus was constructed at the Ames Laboratory of the USAEC and has been described elsewhere.[18] Diffraction patterns were recorded on 4 × 5 in. Kodak process plates at camera distances of 11 and 21 cm with an r^3 sector. Plates were developed at 68°F for 5 min with Kodak D-11 developer.

The AsF_3 sample was contained in a Monel tank, and the AsF_5 was contained in a steel cylinder. The gases were introduced into the diffraction unit *via* Monel tubing and valves through a nickel nozzle with a throat about 0.7 mm long and 0.29 mm in diameter. Exposure times were of the order of 0.5 sec at the 21-cm camera distance and 2 sec at the 11-cm camera distance, with the sample pressures about 20 Torr and a beam current of 0.42 μA. The pressure in the diffraction chamber was maintained at about 3×10^{-5} Torr during introduction of the gases.

Four apparently flawless plates for each compound at each

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[1] This work was supported by a grant from the National Science Foundation.

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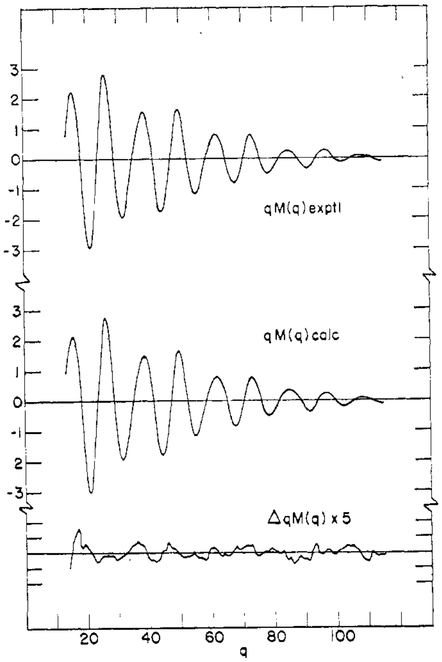

Figure 1.—Molecular intensity curves for AsF_3: $\Delta qM(q) = qM(q)_{\text{exptl}} - qM(q)_{\text{calcd}}$.

camera distance were selected for microphotometer measurements. Readings were made at $^1/_8$-mm intervals across the full diameter of the plate spinning at 180 rpm, and either the even or the odd $^1/_8$-mm readings were selected for subsequent calculations. Microphotometer readings were converted to optical densities, and a correction was applied for the radial variation of plate sensitivity. This corrected optical density varied from about 0.2 to 0.8. Exposure values were derived from the corrected optical density by applying an emulsion calibration $E = A + 0.05A^3$. From exposure values a leveled intensity function was computed and corrected for sector irregularities and extraneous scattering as described elsewhere.[19,20] The leveling of experimental intensities was carried out with the elastic scattering factors of Strand and Bonham[21] and inelastic scattering factors of Heisenberg and Bewilogua.[22] All work after calculation of the leveled intensities, however, was based on scattering factors due to Cox and Bonham[23] and to Tavard.[24]

Analysis of Data

Leveled experimental intensities were converted to reduced molecular intensities, and these were interpolated, merging the data from the 11- and 21-cm camera distances to integral values of the scattering variable, q, for a least-squares comparison between experimental and theoretical points in which the weighting function was

$$W(q) = C - e^{-\alpha(q-q_A)^2} \qquad (1)$$

with $\alpha = 0.005$, $q_A = 10.0$, and $C = 1.2$. The results were insensitive to the weighting function; its primary purpose was to weight down the first few accessible data points.

Experimental radial distribution functions taking into account the effect of anharmonicity,[20,25] integral termination errors,[19] scattering by planetary electrons,[26] and the failure of the Born approximation[27] were calculated with theoretical data for q = 0–15 blended into experimental data for q = 10–125. The value of b in the damping factor e^{-bs^2} was taken to be 0.00125.

Least-squares analyses of the experimental intensity and radial distribution function were carried out with computer programs originally devised by Boates,[28] which constrain the descriptive model to change so that the complete set of molecular parameters remains geometrically consistent.

Asymmetry constants a were estimated[29] to be about 1.7 Å^{-1} for arsenic–fluorine bonded distances and were assumed to be 1.0 Å^{-1} for fluorine–fluorine nonbonded distances. Corrections for shrinkage effects[30] were estimated from calculations on octahedral and tetrahedral[31] fluorides and by comparison with values for PF_3 and PF_5[31] to be 0.0015 Å for the $F \cdots F$ distance in AsF_3 and 0.0035 Å for $F_{ax} \cdots F_{ax}$, 0.0008 Å for $F_{ax} \cdots F_{eq}$, and 0.0007 Å for $F_{eq} \cdots F_{eq}$ in AsF_5.

In determining the amplitudes of vibration for the arsenic–fluorine bonds in AsF_5, since it is not possible to establish independent values from the bonded peak in the radial distribution function alone, an extension[32] of Badger's rule,[33] which relates force constants to bond lengths, was used to estimate roughly the shift in amplitude expected to accompany the observed difference between axial and equatorial bond lengths. Even with this constraint on amplitudes imposed, strong correlations between the bonded amplitude, the Born correction, the index of resolution, and the difference between axial and equatorial bonds, coupled with small systematic errors,[34] led to a convergence at an unreasonably large bonded amplitude in intensity analyses. Therefore, analyses were also run imposing a fixed bonded amplitude in accord with that determined for AsF_3. It is probable that the latter analyses yield more reliable values for the other parameters.

Results

Figures 1 and 2 show molecular intensity curves determined for AsF_3 and AsF_5. These intensity curves are in each case a composite of the curves determined for the 21- and 11-cm data, blended in the overlap region. Indices of resolution $R = M(q)_{\text{exptl}}/M(q)_{\text{calcd}}$ were 1.05

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TABLE I

MOLECULAR PARAMETERS DETERMINED FOR AsF_3 AND AsF_5[a]

Arsenic Trifluoride[b]

Parameter	r_g	l_g Obsd	l_g Calcd[c]
As–F	1.7063 ± 0.0006 (0.001) (0.002)	0.048 ± 0.0007 (0.001) (0.003)	0.043
F···F	2.5376 ± 0.0017 (0.002)	0.078 ± 0.0014 (0.002) (0.003)	0.078
F–As–F[d]	96.16 ± 0.05 (0.13) (0.20)		
I_{xx}(microwave)	85.9635		
I_{xx}(electron diffraction)[b]	85.18 (from estimated r_z parameters) 85.92 (from r_g(As–F) and α_z)		

Arsenic Pentafluoride

Parameter	r_g	l_g Obsd[e]	l_g Calcd[f]	l_g Calcd[g]
As–F (mean distance)	1.678 ± 0.0011 (0.001) (0.002)	[0.050]		
(As–F_{ax}) − (As–F_{eq})	0.055 ± 0.0067 (0.010)			
As–F_{ax}	1.711 ± 0.0047 (0.005)	[0.052]	0.046	0.041
As–F_{eq}	1.656 ± 0.0032 (0.004)	[0.049]	0.044	0.039
F_{ax}···F_{eq}	2.380 ± 0.0026 (0.003)	0.078 ± 0.0021 (0.003)	0.068	0.071
F_{eq}···F_{eq}	2.867 ± 0.006 (0.006)	0.100 ± 0.006 (0.006)	0.083	0.130
F_{ax}···F_{ax}	3.419 ± 0.015 (0.015)	0.082 ± 0.012 (0.012)		0.055

[a] Distances in Å, angles in deg, and I_{xx} in amu Å^2. Uncertainties in parentheses are estimated standard errors including the effects of known systematic errors; where a second, larger value is listed, an arbitrary factor is included because it is believed the original value is unrealistically small. Unparenthesized uncertainties are based solely on random errors inferred from least-squares analyses according to L. S. Bartell in "Physical Methods in Chemistry," A. Weissberger and B. W. Rossiter, Ed., 4th ed, Interscience Publishers, New York, N. Y., in press. Values were estimated by two methods, the larger estimate being quoted. In method 1, based on intensity analyses, the standard error in the ith parameter, θ_i (which may be a distance or an amplitude), was calculated according to $\sigma(\theta_i) = \sqrt{\mathcal{R}_i}\sigma^\circ(\theta_i)$, where $\sigma^\circ(\theta_i)$ is given by $\sigma^\circ(\theta_i) = [(B^{-1})_{ii}\mathbf{V}'\mathbf{W}\mathbf{V}/(n - m)]^{1/2}$, and $\mathcal{R}_i$ is given by $\mathcal{R}_i = 2\gamma/[\Delta s(\gamma^2 + r_i^2)]$, for the ith peak, where r_i is the position of the ith peak, γ is an intensity correlation parameter found to be about 1 Å, and Δs is the increment between intensity points. In method 2, based on $f(r)$ analyses, the standard errors in bond lengths were calculated from $\sigma(r_i) = [n/(n - m)]^{1/2}[32bL^2]^{1/4}[L^2/(L^2 + 2b)]^{3/4}\sigma(f_i)/f_m$, and the standard errors in the amplitudes were calculated from $\sigma(l_i) = [2n/(3\{n - m\})]^{1/2}[L/l][32bL^2]^{1/4}[L^2/(L^2 + 2b)]^{5/4}\sigma(f_i)/f_m$, where $\sigma(f_i)$ is the characteristic root-mean-square noise in $f(r)$ at r_i, and $L^2 = 2b + \delta^2 + l^2$, where b is the constant in the damping factor e^{-bs^2}, l is the amplitude associated with r_i, and δ is a phase shift term $\Delta\eta/s$ evaluated at $s = 1.2/l$. [b] By analogy with PF_3 as treated in ref g it may be estimated that the r_z bond length is about 0.007 Å shorter than the r_g bond length. Since r_z should be closer than r_g to a spectroscopic bond length, it is evident from the tabulated moments of inertia that a larger discrepancy exists between the microwave and diffraction results than would be expected from the estimated errors. Even granting the likely explanation that the diffraction data contain a systematic error of several parts per thousand, there seems no reason to doubt the validity of our principal conclusions. [c] See A. Muller, B. Krebs, and C. J. Peacock, *Z. Naturforsch.*, **23,** 1024 (1968). [d] Corrected for shrinkage effect. [e] Values in brackets were assumed. [f] See G. Nagarajan and J. R. Durig, *Bull. Soc. Roy. Soc. Liege*, **36,** 334 (1967). [g] See S. J. Cyvin and J. Brunvoll, *J. Mol. Struct.*, **3,** 151 (1969).

TABLE II

COMPARISON OF RESULTS OBTAINED BY ANALYSIS OF THE RADIAL DISTRIBUTION FUNCTION AND INTENSITY DATA FOR AsF_3 AND AsF_5[a]

Arsenic Trifluoride

	As–F, r_g	F···F, r_g	Angle F–As–F[b]	l_g(As–F)[c]	l_g(F···F)	σ[d]
Intens (21 cm)	1.7060	2.5381	96.20	0.0511	0.0729	0.0020
Intens (11 cm)	1.7069	2.5417	96.41	0.0510	0.0810	0.0004
Intens (blended)	1.7056	2.5386	96.26	0.0480	0.0755	0.0014
Radial distribution function	1.7076	2.5357	95.96	0.0490	0.0791	0.0064

Arsenic Pentafluoride

	As–F(mean), r_g	(As–F_{ax}) − (As–F_{eq})	As–F,[c] l_g	F_{ax}···F_{eq}, l_g	F_{eq}···F_{eq}, l_g	F_{ax}···F_{ax}, l_g	σ[d]
Bonded Amplitude Varied							
Intens (21 cm)	1.6789	0.029	0.060	0.078	0.110	0.072	0.0014
Intens (11 cm)	1.6763	0.034	0.059	0.074	0.096	0.071	0.0007
Intens (blended)	1.6783	0.029	0.060	0.077	0.110	0.065	0.0010
Radial distribution function	1.6781	0.051	0.054	0.080	0.101	0.082	0.0093
Bonded Amplitude Fixed							
Intens (21 cm)	1.6787	0.045	(0.050)	0.076	0.105	0.080	0.0052
Intens (11 cm)	1.6777	0.044	(0.050)	0.075	0.094	0.078	0.0041
Intens (blended)	1.6778	0.058	(0.050)	0.075	0.110	0.084	0.0040
Radial distribution function	1.6781	0.059	(0.050)	0.080	0.102	0.094	0.0091

[a] Distances in Å; angles in deg. [b] Corrected for shrinkage effect. [c] l_g(As–F_{ax}) − l_g(As–F_{eq}) was fixed at 0.003 Å. [d] $\sigma(f/f_{max})$ for the radial distribution function; $\sigma(I)/I$ for the intensity function.

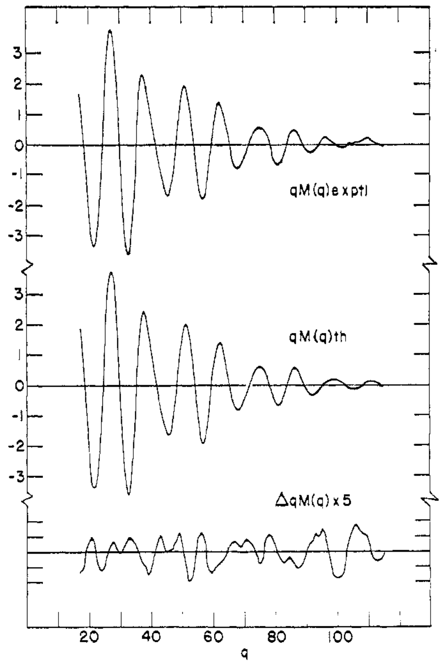

Figure 2.—Molecular intensity curves for AsF_5: $\Delta qM(q) = qM(q)_{\text{exptl}} - qM(q)_{\text{calcd}}$.

and 1.03 for the 21- and 11-cm AsF_3 data. The corresponding indices of resolution for AsF_5 were 0.93 and 0.93. The radial distribution functions for the two molecules are illustrated in Figures 3 and 4.

The results of our investigation are summarized in Table I. Experimental data were analyzed by least-squares fittings of the radial distribution function, the intensity for each camera distance, and a blend of the two camera distances. Values of parameters obtained by the various methods are compared in Table II. The error matrices[35] computed during the final least-squares runs on the blended intensity are reproduced in Tables III and IV. Since they were based on the nonoptimum diagonal weight matrix embodied in eq 1, their elements do not represent bona fide standard errors. The principal utility of the error matrices is in deducing correlations among the different parameters. Listings of the experimental leveled intensity and background as functions of s for the 21- and 11-cm camera distances are given in Tables V and VI.

TABLE III

ERROR MATRIX FOR AsF_3[a]

	r(As–F)	*r*(F···F)	*l*(As–F)	*l*(F···F)	*R*
r(As–F)	4.7	−2.7	1.1	1.8	4.7
r(F···F)		19.4	−4.5	−5.8	−12.5
l(As–F)			10.0	7.1	20.3
l(F···F)				23.3	20.6
R					58.4

[a] Values are $\times 10^4$. Based on 103 intensity values interpolated from 216 data points. Units for the distances and amplitudes are in Å; the index of resolution *R* is dimensionless. Matrix elements are given by $\sigma_{ij} = \text{sign}[(B^{-1})_{ij}]\{|(B^{-1})_{ij}\mathbf{V}'\mathbf{W}\mathbf{V}/(n - m)\}^{1/2}$, where the notation corresponds to that of O. Bastiansen, L. Hedberg, and K. Hedberg, *J. Chem. Phys.*, **27**, 1311 (1957).

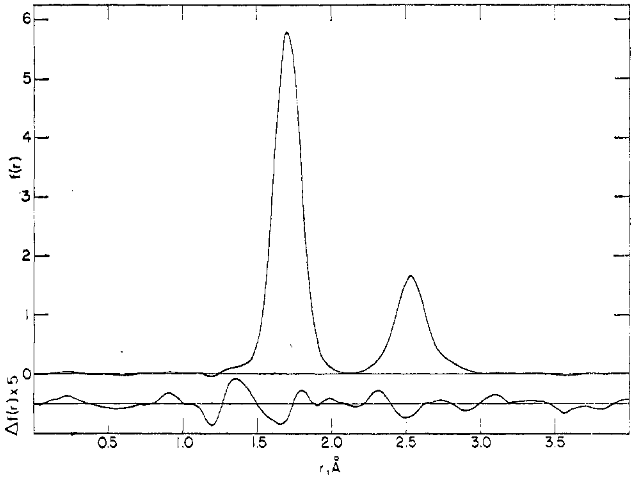

Figure 3.—Experimental radial distribution function for AsF_3: $\Delta f(r) = f(r)_{\text{exptl}} - f(r)_{\text{calcd}}$.

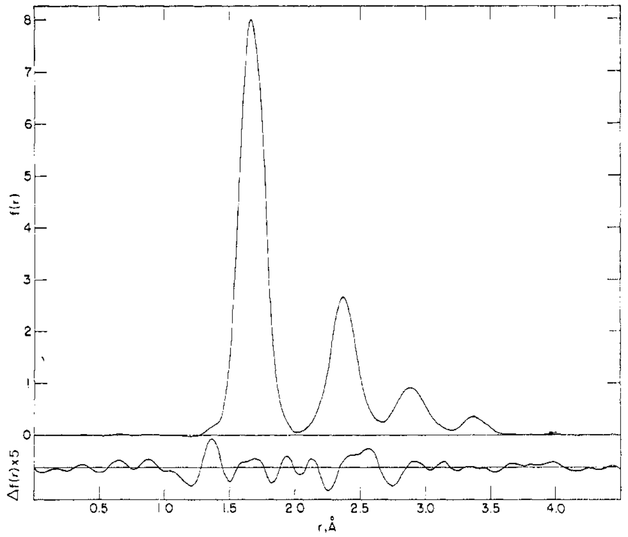

Figure 4.—Experimental radial distribution function for AsF_5: $\Delta f(r) = f(r)_{\text{exptl}} - f(r)_{\text{calcd}}$.

Discussion

Mean amplitudes of vibration for AsF_3 at 298°K have been calculated from vibrational frequency data by Sundaram[36] (0.0425 and 0.0772 Å for the As–F and F···F amplitudes, respectively), Venkateswarlu, *et al.*[37] (0.0725 and 0.0917 Å), and Muller, *et al.*[38] (0.045 and 0.078 Å, by a somewhat different method). The present experimental values of 0.048 and 0.078 Å agree much more closely with the results of Sundaram and Muller than with the other calculation.

Nagarajan and Durig[39] and Cyvin and Brunvoll[40] have published computed values of the amplitudes of vibrations of AsF_5 and PF_5. Uncertainties exist in the

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TABLE IV

ERROR MATRIX FOR AsF_5[a]

	r(As–F) (mean)	r(As–F_{ax}) − r(As–F_{eq})	l(bonded)[b]	l($F_{ax}\cdots F_{eq}$)	l($F_{eq}\cdots F_{eq}$)	l($F_{ax}\cdots F_{ax}$)	R
r(As–F) (mean)	4.0	1.5	−2.3	−0.5	−3.5	−3.2	1.2
r(As–F_{ax}) − r(As–F_{eq})		22.5	−23.9	−6.4	1.2	14.4	−28.6
l(bonded)[b]			16.9	11.3	3.4	−12.4	28.2
l($F_{ax}\cdots F_{eq}$)				15.9	−5.8	2.7	25.2
l($F_{eq}\cdots F_{eq}$)					47.7	−25.1	1.2
l($F_{ax}\cdots F_{ax}$)						143.6	15.7
R							70.0

[a] Values are $\times 10^4$. Based on 109 intensity values interpolated from 218 data points. See Table III for conventions. [b] l(As–F_{ax}) − l(As–F_{eq}) was fixed at 0.003 Å.

TABLE V

EXPERIMENTAL LEVELED INTENSITY AND BACKGROUND DATA FOR AsF_3[a]

S	$I_0(S)$	B(S)	S	$I_0(S)$	B(S)	S	$I_0(S)$	B(S)	S	$I_0(S)$	B(S)	S	$I_0(S)$	B(S)
4.078	2.6041		4.201	2.6548		4.325	2.7160		4.448	2.7428		4.571	2.7933	
4.695	2.8209		4.818	2.8283		4.942	2.8232		5.065	2.7981		5.188	2.7574	
5.311	2.7107		5.435	2.6382		5.558	2.5626		5.681	2.4769		5.804	2.3945	
5.928	2.3164	2.4726	6.051	2.2409	2.4690	6.174	2.1775	2.4655	6.297	2.1303	2.4621	6.420	2.0986	2.4587
6.543	2.0883	2.4555	6.666	2.0944	2.4523	6.790	2.1234	2.4492	6.913	2.1679	2.4461	7.036	2.2255	2.4431
7.159	2.2912	2.4402	7.282	2.3635	2.4373	7.405	2.4394	2.4344	7.527	2.5118	2.4316	7.650	2.5749	2.4288
7.773	2.6280	2.4260	7.896	2.6658	2.4232	8.019	2.6882	2.4203	8.142	2.6949	2.4175	8.265	2.6873	2.4148
8.387	2.6639	2.4121	8.510	2.6307	2.4094	8.633	2.5884	2.4068	8.755	2.5401	2.4043	8.878	2.4865	2.4018
9.001	2.4330	2.3994	9.123	2.3841	2.3970	9.246	2.3404	2.3948	9.368	2.3029	2.3926	9.491	2.2735	2.3905
9.613	2.2507	2.3886	9.736	2.2386	2.3868	9.858	2.2321	2.3850	9.981	2.2349	2.3833	10.103	2.2408	2.3817
10.225	2.2579	2.3802	10.348	2.2691	2.3787	10.470	2.2882	2.3772	10.592	2.3074	2.3758	10.714	2.3272	2.3744
10.837	2.3469	2.3730	10.959	2.3650	2.3717	11.081	2.3831	2.3704	11.203	2.3991	2.3692	11.325	2.4142	2.3680
11.447	2.4276	2.3669	11.569	2.4364	2.3658	11.691	2.4461	2.3648	11.813	2.4532	2.3637	11.934	2.4562	2.3628
12.056	2.4573	2.3618	12.178	2.4535	2.3608	12.300	2.4466	2.3598	12.422	2.4376	2.3589	12.543	2.4247	2.3580
12.665	2.4104	2.3572	12.786	2.3928	2.3565	12.908	2.3730	2.3558	13.029	2.3524	2.3553	13.151	2.3309	2.3548
13.272	2.3104	2.3544	13.394	2.2921	2.3541	13.515	2.2764	2.3538	13.636	2.2634	2.3537	13.758	2.2580	2.3536
13.879	2.2553	2.3536	14.000	2.2567	2.3537	14.121	2.2628	2.3538	14.242	2.2752	2.3540	14.363	2.2911	2.3543
14.484	2.3104	2.3547	14.605	2.3299	2.3551	14.726	2.3501	2.3557	14.847	2.3723	2.3563	14.968	2.3921	2.3570
15.089	2.4105	2.3578	15.209	2.4264	2.3586	15.330	2.4373	2.3594	15.451	2.4431	2.3603	15.571	2.4454	2.3611
15.692	2.4444	2.3620	15.812	2.4385	2.3629	15.933	2.4317	2.3639	16.053	2.4191	2.3649	16.174	2.4062	2.3659
16.294	2.3916	2.3669	16.414	2.3784	2.3680	16.534	2.3640	2.3691	16.655	2.3523	2.3702	16.775	2.3413	2.3714
16.895	2.3342	2.3727	17.015	2.3284	2.3739	17.135	2.3261	2.3752	17.255	2.3245	2.3765	17.374	2.3265	2.3779
17.494	2.3299	2.3793	17.614	2.3362	2.3807	17.734	2.3416	2.3822	17.853	2.3494	2.3837	17.973	2.3561	2.3852
18.093	2.3653	2.3868	18.212	2.3738	2.3884	18.331	2.3830	2.3900	18.451	2.3911	2.3917	18.570	2.3987	2.3934
18.689	2.4054	2.3951	18.809	2.4104	2.3969	18.928	2.4160	2.3987	19.047	2.4202	2.4006	19.166	2.4236	2.4024
19.285	2.4265		19.404	2.4279		19.523	2.4277		19.641	2.4268		19.760	2.4259	
19.879	2.4236		19.998	2.4214		20.116	2.4188		20.235	2.4182		20.353	2.4160	
20.471	2.4118		20.590	2.4093		20.708	2.4043		20.826	2.4025		20.944	2.4039	
21.063	2.4054		21.181	2.4070		21.299	2.4101		21.416	2.4173				

S	$I_0(S)$	B(S)	S	$I_0(S)$	B(S)	S	$I_0(S)$	B(S)	S	$I_0(S)$	B(S)	S	$I_0(S)$	B(S)
8.503	2.8339		8.738	2.7230		8.973	2.6359		9.208	2.5414		9.443	2.4683	
9.677	2.4221		9.912	2.4061		10.146	2.4171		10.380	2.4475		10.614	2.4744	
10.848	2.5208		11.082	2.5539		11.316	2.5876		11.550	2.6128		11.783	2.6330	
12.016	2.6385		12.250	2.6315		12.483	2.6145		12.716	2.5853		12.948	2.5446	
13.181	2.5041		13.414	2.4662		13.646	2.4384		13.878	2.4260		14.110	2.4331	
14.342	2.4596	2.5396	14.574	2.4996	2.5416	14.805	2.5425	2.5436	15.037	2.5824	2.5457	15.268	2.6125	2.5479
15.499	2.6282	2.5502	15.730	2.6284	2.5525	15.961	2.6152	2.5550	16.191	2.5928	2.5576	16.421	2.5671	2.5602
16.652	2.5412	2.5630	16.882	2.5246	2.5658	17.111	2.5160	2.5687	17.341	2.5142	2.5717	17.570	2.5236	2.5747
17.800	2.5390	2.5777	18.029	2.5563	2.5809	18.258	2.5749	2.5841	18.486	2.5934	2.5875	18.715	2.6111	2.5909
18.943	2.6243	2.5946	19.171	2.6333	2.5983	19.399	2.6379	2.6022	19.626	2.6392	2.6061	19.854	2.6357	2.6101
20.081	2.6312	2.6142	20.308	2.6223	2.6183	20.535	2.6134	2.6224	20.761	2.6055	2.6265	20.987	2.6009	2.6307
21.213	2.6014	2.6348	21.439	2.6063	2.6390	21.665	2.6156	2.6431	21.890	2.6306	2.6472	22.115	2.6481	2.6513
22.340	2.6651	2.6554	22.565	2.6797	2.6594	22.789	2.6906	2.6635	23.014	2.6962	2.6675	23.238	2.6954	2.6714
23.461	2.6922	2.6754	23.685	2.6878	2.6794	23.908	2.6823	2.6834	24.131	2.6786	2.6874	24.353	2.6773	2.6915
24.576	2.6781	2.6956	24.798	2.6834	2.6998	25.020	2.6893	2.7040	25.242	2.6979	2.7083	25.463	2.7068	2.7127
25.684	2.7158	2.7173	25.905	2.7256	2.7220	26.126	2.7337	2.7267	26.346	2.7393	2.7315	26.566	2.7449	2.7362
26.786	2.7508	2.7410	27.005	2.7529	2.7455	27.225	2.7552	2.7501	27.444	2.7591	2.7546	27.662	2.7607	2.7591
27.881	2.7614	2.7637	28.099	2.7625	2.7684	28.317	2.7650	2.7732	28.534	2.7679	2.7781	28.751	2.7735	2.7831
28.968	2.7816	2.7881	29.185	2.7900	2.7933	29.401	2.7975	2.7985	29.617	2.8056	2.8039	29.833	2.8137	2.8093
30.049	2.8227	2.8148	30.264	2.8276	2.8204	30.479	2.8348	2.8261	30.693	2.8390	2.8318	30.908	2.8423	2.8376
31.122	2.8447	2.8435	31.335	2.8483	2.8494	31.549	2.8520	2.8553	31.762	2.8566	2.8613	31.975	2.8617	2.8673
32.187	2.8678	2.8733	32.399	2.8748	2.8793	32.611	2.8815	2.8854	32.822	2.8898	2.8914	33.034	2.8967	2.8976
33.244	2.9037	2.9037	33.455	2.9119	2.9098	33.665	2.9179	2.9160	33.875	2.9239	2.9222	34.085	2.9302	2.9285
34.294	2.9366	2.9349	34.503	2.9421	2.9414	34.711	2.9516	2.9481	34.920	2.9568	2.9549	35.128	2.9629	2.9619
35.335	2.9697	2.9689	35.542	2.9756	2.9761	35.749	2.9825	2.9833	35.956	2.9897	2.9907	36.162	2.9972	2.9982
36.368	3.0039	3.0058	36.574	3.0115	3.0135	36.779	3.0192	3.0213	36.984	3.0257	3.0292	37.189	3.0334	3.0372
37.393	3.0411		37.597	3.0509		37.800	3.0602		38.003	3.0716		38.206	3.0833	
38.409	3.0930		38.611	3.1030		38.813	3.1101		39.014	3.1205		39.215	3.1330	
39.416	3.1461													

[a] Top, 21-cm-camera data; bottom, 11-cm-camera data. The function $M(q)$ is given by $(I_0/B) - 1$.

frequency assignments for both molecules.[40,41] The present data may be of some utility in the resolution of ambiguities. In particular, the pattern of experimental amplitudes for the various interatomic pairs closely follows that observed for PF_5[16] and PCl_5.[42] In the latter two molecules the ambiguity in assigning the e''

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(41) P. C. Van DerVoorn, K. F. Purcell, and R. S. Drago, *J. Chem. Phys.*, **43**, 3457 (1965); **48**, 3837 (1968); R. M. Dieters and R. R. Holmes, *ibid.*, **48**, 4796 (1968), and references therein.

(42) W. J. Adams and L. S. Bartell, unpublished results.

TABLE VI

EXPERIMENTAL LEVELED INTENSITY AND BACKGROUND DATA FOR AsF_5[a]

S	$I_0(S)$	B(S)	S	$I_0(S)$	B(S)	S	$I_0(S)$	B(S)	S	$I_0(S)$	B(S)	S	$I_0(S)$	B(S)
3.953	2.2133		4.077	2.3042		4.200	2.3686		4.324	2.4325		4.447	2.4730	
4.570	2.5274		4.694	2.5584		4.817	2.5762		4.940	2.5748		5.064	2.5594	
5.187	2.5336	2.2772	5.310	2.5005	2.2807	5.433	2.4504	2.2842	5.557	2.4010	2.2877	5.680	2.3390	2.2910
5.803	2.2801	2.2943	5.926	2.2212	2.2976	6.049	2.1617	2.3008	6.173	2.1065	2.3039	6.296	2.0594	2.3070
6.419	2.0213	2.3100	6.542	1.9969	2.3129	6.665	1.9832	2.3158	6.788	1.9860	2.3187	6.911	2.0048	2.3215
7.034	2.0366	2.3242	7.157	2.0806	2.3268	7.280	2.1371	2.3294	7.403	2.2019	2.3319	7.526	2.2726	2.3345
7.649	2.3453	2.3369	7.771	2.4161	2.3394	7.894	2.4821	2.3418	8.017	2.5408	2.3442	8.140	2.5900	2.3465
8.263	2.6257	2.3489	8.385	2.6477	2.3512	8.508	2.6561	2.3536	8.631	2.6492	2.3561	8.753	2.6287	2.3586
8.876	2.5947	2.3611	8.999	2.5487	2.3636	9.121	2.4979	2.3660	9.244	2.4386	2.3685	9.366	2.3797	2.3710
9.489	2.3209	2.3734	9.611	2.2667	2.3758	9.734	2.2201	2.3783	9.856	2.1829	2.3807	9.978	2.1577	2.3830
10.101	2.1453	2.3854	10.223	2.1449	2.3877	10.345	2.1596	2.3899	10.467	2.1858	2.3922	10.590	2.2206	2.3944
10.712	2.2646	2.3967	10.834	2.3128	2.3989	10.956	2.3622	2.4011	11.078	2.4097	2.4033	11.200	2.4533	2.4055
11.322	2.4898	2.4077	11.444	2.5182	2.4099	11.566	2.5371	2.4122	11.688	2.5485	2.4143	11.810	2.5518	2.4164
11.932	2.5480	2.4185	12.053	2.5380	2.4206	12.175	2.5244	2.4227	12.297	2.5096	2.4249	12.419	2.4951	2.4271
12.540	2.4815	2.4294	12.662	2.4687	2.4317	12.783	2.4585	2.4341	12.905	2.4497	2.4365	13.026	2.4421	2.4391
13.148	2.4364	2.4417	13.269	2.4292	2.4446	13.391	2.4229	2.4477	13.512	2.4163	2.4508	13.633	2.4087	2.4541
13.754	2.4017	2.4574	13.876	2.3956	2.4608	13.997	2.3901	2.4643	14.118	2.3870	2.4679	14.239	2.3874	2.4715
14.360	2.3914	2.4751	14.481	2.3989	2.4789	14.602	2.4096	2.4826	14.723	2.4245	2.4864	14.844	2.4430	2.4903
14.964	2.4646	2.4942	15.085	2.4872	2.4981	15.206	2.5116	2.5020	15.327	2.5358	2.5060	15.447	2.5554	2.5100
15.568	2.5750	2.5140	15.688	2.5917	2.5180	15.809	2.6038	2.5220	15.929	2.6138	2.5261	16.050	2.6182	2.5301
16.170	2.6183	2.5342	16.290	2.6149	2.5382	16.410	2.6085	2.5422	16.531	2.5993	2.5460	16.651	2.5878	2.5499
16.771	2.5746	2.5537	16.891	2.5619	2.5576	17.011	2.5482	2.5614	17.131	2.5359	2.5653	17.251	2.5241	2.5692
17.370	2.5155	2.5731	17.490	2.5091	2.5771	17.610	2.5067	2.5810	17.730	2.5073	2.5850	17.849	2.5115	2.5890
17.969	2.5194	2.5931	18.088	2.5311	2.5972	18.208	2.5458	2.6013	18.327	2.5632	2.6055	18.447	2.5824	2.6098
18.566	2.6008	2.6141	18.685	2.6199	2.6184	18.804	2.6375	2.6228	18.923	2.6545	2.6273	19.042	2.6692	2.6318
19.161	2.6809		19.280	2.6894		19.399	2.6967		19.518	2.7001		19.637	2.7011	
19.756	2.7003		19.874	2.6983		19.993	2.6970		20.111	2.6950		20.230	2.6941	
20.348	2.6931		20.467	2.6923		20.585	2.6901		20.703	2.6886		20.822	2.6897	
20.940	2.6937		21.058	2.6990		21.176	2.7048		21.294	2.7128		21.412	2.7232	

S	$I_0(S)$	B(S)	S	$I_0(S)$	B(S)	S	$I_0(S)$	B(S)	S	$I_0(S)$	B(S)	S	$I_0(S)$	B(S)
8.526	3.2844		8.762	3.2163		8.997	3.1301		9.233	2.9853		9.468	2.8326	
9.703	2.6923		9.938	2.5920		10.173	2.5444		10.408	2.5701		10.643	2.6335	
10.878	2.7230		11.112	2.8164		11.346	2.8968		11.581	2.9448		11.815	2.9543	
12.049	2.9327		12.283	2.8953		12.516	2.8540		12.750	2.8175		12.983	2.7816	
13.216	2.7533		13.450	2.7225		13.683	2.6907		13.915	2.6570		14.148	2.6344	
14.380	2.6277		14.613	2.6385		14.845	2.6671		15.077	2.7072		15.309	2.7517	
15.540	2.7920	2.7472	15.772	2.8214	2.7459	16.003	2.8344	2.7447	16.234	2.8305	2.7436	16.465	2.8124	2.7427
16.696	2.7843	2.7419	16.927	2.7506	2.7412	17.157	2.7160	2.7407	17.387	2.6861	2.7404	17.617	2.6682	2.7403
17.847	2.6636	2.7405	18.077	2.6718	2.7409	18.306	2.6916	2.7414	18.535	2.7188	2.7421	18.764	2.7497	2.7430
18.993	2.7756	2.7440	19.222	2.7943	2.7452	19.450	2.8018	2.7465	19.678	2.7991	2.7479	19.906	2.7913	2.7494
20.134	2.7784	2.7510	20.361	2.7647	2.7526	20.589	2.7497	2.7542	20.816	2.7399	2.7559	21.043	2.7318	2.7574
21.269	2.7281	2.7590	21.496	2.7307	2.7606	21.722	2.7350	2.7622	21.948	2.7446	2.7638	22.173	2.7544	2.7654
22.399	2.7644	2.7669	22.624	2.7725	2.7684	22.849	2.7806	2.7699	23.074	2.7851	2.7715	23.298	2.7898	2.7730
23.523	2.7917	2.7746	23.747	2.7937	2.7762	23.970	2.7951	2.7778	24.194	2.7955	2.7795	24.417	2.7911	2.7812
24.640	2.7848	2.7830	24.863	2.7778	2.7849	25.085	2.7717	2.7867	25.307	2.7682	2.7887	25.529	2.7683	2.7906
25.751	2.7725	2.7927	25.972	2.7803	2.7948	26.193	2.7899	2.7970	26.414	2.8006	2.7992	26.635	2.8102	2.8014
26.855	2.8166	2.8038	27.075	2.8203	2.8061	27.295	2.8216	2.8086	27.514	2.8217	2.8111	27.734	2.8189	2.8137
27.952	2.8169	2.8163	28.171	2.8159	2.8189	28.389	2.8146	2.8215	28.607	2.8157	2.8242	28.825	2.8174	2.8269
29.043	2.8213	2.8296	29.260	2.8266	2.8324	29.477	2.8310	2.8351	29.693	2.8374	2.8378	29.909	2.8436	2.8406
30.125	2.8479	2.8434	30.341	2.8514	2.8459	30.556	2.8526	2.8485	30.771	2.8542	2.8511	30.986	2.8548	2.8538
31.201	2.8572	2.8566	31.415	2.8599	2.8595	31.629	2.8627	2.8625	31.842	2.8642	2.8659	32.055	2.8677	2.8696
32.268	2.8723	2.8735	32.481	2.8763	2.8775	32.693	2.8810	2.8817	32.905	2.8856	2.8859	33.117	2.8892	2.8903
33.328	2.8941	2.8947	33.539	2.8985	2.8991	33.750	2.9025	2.9036	33.960	2.9079	2.9081	34.170	2.9134	2.9126
34.380	2.9186	2.9172	34.589	2.9235	2.9218	34.798	2.9269	2.9264	35.007	2.9310	2.9306	35.215	2.9343	2.9348
35.423	2.9381	2.9389	35.631	2.9429	2.9432	35.838	2.9481	2.9476	36.045	2.9523	2.9523	36.252	2.9555	2.9572
36.458	2.9627	2.9623	36.664	2.9675	2.9683	36.870	2.9746	2.9746	37.075	2.9823	2.9812	37.280	2.9887	2.9881
37.485	2.9934	2.9952	37.689	3.0010	3.0026	37.893	3.0094	3.0102	38.097	3.0175	3.0181	38.300	3.0280	3.0262
38.503	3.0376	3.0345	38.705	3.0443	3.0428	38.908	3.0484	3.0512	39.109	3.0575	3.0595	39.311	3.0676	3.0678
39.512	3.0782													

[a] Top, 21-cm-camera data; bottom, 11-cm-camera data. The function $M(q)$ is given by $(I_0/B) - 1$.

bending frequencies seems to be resolved by the diffraction results in favor of the axial frequency exceeding the equatorial frequency. Presumably, the same result will hold for AsF_5.

The difference between axial and equatorial bond lengths in AsF_5, 0.055 Å, is not significantly different from the 0.043-Å value reported by Hansen and Bartell[16] for the corresponding quantity in PF_5. Our AsF_3 and AsF_5 results show clearly that the pentafluoride compound has a shorter average bond length by about 0.03 Å than the trifluoride, even though the bonds are "weaker," on the average, according to the bond energies.[15] Similarly, the work of Morino, Kuchitsu, and Moritani[43] and of Hansen and Bartell[16] reveals that the thermochemically weaker bonds[17] in PF_5 are about 0.019 Å shorter, on the average, than in PF_3.

The bond angle published by Kisliuk and Geschwind[7] for AsF_3 was too large by approximately 6° and made it appear as if the AsF_3 bond angle was the largest in the series AsF_3, $AsCl_3$, $AsBr_3$, AsI_3. Our work shows it is in fact the smallest angle in the series. At the time our study began, it was also thought that the F–P–F bond angle in PF_3 fitted a similar pattern, being the largest in the series PF_3, PCl_3, PBr_3, PI_3. However, the recent investigation of PF_3[43] has shown that the fluoride has the smallest bond angle in the phosphorus series, just as we have found it has in the arsenic series.

Some inconsistencies arose in a treatment of the force field of AsF_3 by Hoskins and Lord[44] when the structure parameters reported by Kisliuk and Geschwind[7] were adopted. Subsequently, Mirri[45] pointed out that the inconsistencies could be resolved if the As–F distance

(43) Y. Morino, K. Kuchitsu, and T. Moritani, *Inorg. Chem.*, **8**, 867 (1969).

(44) L. C. Hoskins and R. C. Lord, *J. Chem. Phys.*, **43**, 155 (1965).

(45) A. M. Mirri, *ibid.*, **47**, 2823 (1967).

and F–As–F angle were revised to 1.708 Å and 98°. These revised parameters are very close to those found in the present investigation.

If one of the fluorine atoms in AsF_3 is replaced by the less electronegative methyl group, the F–As–F angle changes very little[46] (96.2 ± 0.2° in AsF_3, 96 ± 4° in CH_3AsF_2). Methyl substitution appreciably influences the lengths of adjacent As–F bonds, however, increasing them from 1.706 Å to approximately 1.74 Å. Such a change is expected on the basis of the primary rules of Gillespie's valence shell–electron repulsion model.[47] On the other hand, Gillespie introduced a subrule to account for structures of the group V trihalides, arguing in favor of appreciable double-bond character for the As–F and P–F bonds in order to rationalize the apparently anomalous experimental F–X–F bond angles of 102 and 104° for AsF_3 and PF_3, respectively. It is now clear that the bond angles of the two compounds are not anomalously large, but rather are the smallest in their respective series. Therefore, the Gillespie subrule loses some of its significance.

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[46] L. J. Nugent and C. D. Cornwell, NBS Report 7099, March 1961; *J. Chem. Phys.*, **37**, 523 (1962).

[47] R. J. Gillespie, *J. Chem. Educ.*, **40**, 295 (1963); *Angew. Chem.*, **79**, 885 (1967); *Angew. Chem., Intern. Ed. Engl.*, **6**, 819 (1967); *J. Am. Chem. Soc.*, **82**, 5978 (1960).

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The Cl_2F^+ and Cl_3^+ Cations

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The Raman spectra of the 2:1 adducts of ClF with AsF_5 and BF_3 show that the cation has the asymmetric $ClClF^+$ structure and not the symmetric $ClFCl^+$ structure previously reported.[1] The AsF_6^- salt of Cl_3^+ has been prepared from ClF, Cl_2, and AsF_5. Low-temperature Raman spectra show that Cl_3^+ has C_{2v} symmetry, and simple valence force constants have been calculated.

In a recent paper[1] Christe and Sawodny showed that ClF forms 2:1 adducts with the Lewis acids AsF_5 and BF_3. Low-temperature infrared spectra showed that these are salts of AsF_6^- and BF_4^-. Three frequencies common to both compounds of 586, 529, and 293 cm^{-1} were assigned to the cation and it was concluded that the cation probably had the symmetric $ClFCl^+$ structure. We report now the low-temperature Raman spectra of these salts and the preparation of the $Cl_3^+AsF_6^-$ salt and its vibrational frequencies.

The bands observed in the Raman spectra of $Cl_2F^+AsF_6^-$ and $Cl_2F^+BF_4^-$ are given in Tables I and II, together with our assignments. These differ from the assignments of Christe and Sawodny as we observe a strong Raman band at 744 cm^{-1} in both salts (Figure 1), which was not seen in the infrared spectra. This we assign to the Cl–F stretch in the unsymmetrical $ClClF^+$ cation. The intense Raman peaks at 516 and 540 cm^{-1} in the BF_4^- salt and 528 and 535 cm^{-1} in the AsF_6^- salt can be assigned to the Cl–Cl stretch.

In the AsF_6^- salt Christe and Sawodny assigned infrared bands at 586 and 593 cm^{-1} to ν_2(asymmetric stretch) of $ClFCl^+$ and bands at 569 and 555 cm^{-1} to the overtone of the bending mode of Cl_2F^+ at 293 cm^{-1} whereas we assign the Raman bands at 563 and 581 cm^{-1} to $\nu_2(E_g)$ of AsF_6^-. The splitting of the Raman band is attributed to the removal of the degeneracy in the solid state probably as a consequence of fluorine bridging. This also causes ν_2 to be active in the infrared spectrum and accounts for two of the infrared peaks in the band in the region 555–593 cm^{-1}, the remaining two being assigned following Christe and Sawodny to the overtone of ν_3(bend) of $ClClF^+$. Recently[2] we showed that in the salt $ClF_2^+AsF_6^-$ the Raman frequency of 544 cm^{-1} (ir: 520 and 558

TABLE I

INFRARED AND RAMAN SPECTRA OF $Cl_2F^+AsF_6^-$

Infrared,[a] cm^{-1}	Raman, $\Delta\nu$, cm^{-1}	Assignment	
		Cl_2F^+	AsF_6^-
258 mw			
293 m	293 299 (20)[b]	ν_3 (bend)	
	375 (12)		ν_5
397 ms			ν_4
514 vw, sh			
520 vw			
527 mw	528 535 (100)	ν_2 (Cl–Cl str)	
535 m			
555 m		2ν_3	ν_2
569 vw	563 (16)		
586 mw	581 (12)		
593 m			
	685 (70)		ν_1
703 vs	744 (78)	ν_1 (Cl–F str)	ν_3

[a] Reference 1. [b] Figures in parentheses give the relative intensities (peak heights) of the observed Raman bands.

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[1] K. O. Christe and W. Sawodny, *Inorg. Chem.*, **8**, 212 (1969).

[2] R. J. Gillespie and M. J. Morton, *ibid.*, **9**, 616 (1970).