IR Spectroscopy of OP−X and Derivatives: Mistaken Identity on a Large Scale

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Previous low resolution gas-phase IR spectra of OP−X and related derivatives generated by pyrolysis are critically examined. Density functional calculations at the B3LYP/aug-cc-pVTZ level have been performed for these and similar benchmark molecules where reliable experimental data exist. These theoretical results, comparison with published high-resolution data, and the reassignment of observed bands to well-known chemical species lead to revisions for OCNCN and total rejection of earlier vibrational assignments for OPCl, OPBr, OPI, OPI_3, $OSbF_3$, $OSbCl_3$, OPCN, OPSCN, NSCN, and NSSCN.

1. Introduction

A host of chemical species, including transient molecules, have been generated by flow pyrolysis and IR spectroscopy is a highly effective tool for probing the products. Pyrolysis is far from being a clean synthesis, however, and there is no guarantee that the target species will be generated. Considerable care is needed to identify all the products, particularly when relying on low resolution IR measurements alone. In that case, it is essential to support new assignments with appropriate theoretical predictions, to compare spectra with those of possible byproducts and to consider whether observed band profiles are consistent with the molecules in question. In this regard, high-resolution measurements are preferable, as the rotational constants that may be derived from them are far less ambiguous. OPF is a case in point. Recent high-resolution FTIR work based on pyrolysis of F_2POPF_2, supported by high level ab initio calculations, revealed that the OP stretch band of OPF is centered at 1297.537 cm^{-1}.[1] An earlier low resolution IR study from the laboratory of Allaf[2] had erroneously assigned a band at 1357 cm^{-1} to this mode. The low resolution work relied on a two-step synthesis, flowing $OPCl_3$(g) over silver at 870 °C to generate OPCl(g), which was to pass through a second furnace containing NaF(s) to produce OPF. Similar reaction schemes involving the generation and subsequent reaction of OPCl were invoked in Allaf's work on OPBr and OPI,[3] OPCN,[4] and OPSCN.[5] The IR spectrum of OPCl reported in these papers, however, casts doubt on the work. A considerable discrepancy exists between the accurate OP stretch band center of OPCl determined by diode laser measurements (1263.007 cm^{-1})[6] and the value of 1273 cm^{-1} quoted by Allaf.[2]

In this paper, we set out to thoroughly assess earlier low resolution IR work on OP−X molecules,[2−5,7] related NS−derivatives NSCN[8] and NSSCN,[9] and antimony oxide trihalides.[10] We employ density functional theory (DFT) calculations to help test the feasibility of vibrational assignments. Such predictions are more reliable when vibrational frequencies are scaled using data from closely related molecules.[11] We have therefore analyzed a data set of molecules possessing CN (including SCN and OCN), OP, NS, CS, NO, MO, and M−X (M = group V atom; X = halide) subunits for which reliable experimental data can provide a benchmark. This theoretical work points to suspect vibrational assignments for a number of molecules. These molecules are further examined here.

2. Computational Details

Density functional theory (DFT) calculations were carried out with the Gaussian 98 suite of programs,[12] using the hybrid Becke3-Lee-Yang-Par functional. Both 6-311+G(d,p) and Dunning's correlation consistent aug-cc-pVTZ basis sets were employed. MP2 calculations were carried out for a limited set of molecules at these basis sets. Finally, MP2 and DFT calculations with a 3-21G** basis were performed to investigate molecules of the class OMX_3 and MX_3 (M = group V atom; X = halide). A search for all PE minima was carried out, and vibrational wavenumber values were computed at these points.

3. DFT Results

The focus on halogenated OP−X derivatives along with $OSbF_3$, $OSbCl_3$, OPCN, OPSCN, NSCN, and NSSCN governed the choice of benchmark molecules. A total of 47 benchmark molecules possessing CN (including SCN and OCN), OP, OAs, OSb, NS, CS, NO, or MX subunits were selected. Some of the smaller molecules have already been examined at high levels of theory, e.g., anharmonic force field analyses for HCN at the CISD level,[13] ClCN at the CCSD(T) level,[14] and FPO at the MP2 level.[1] The present study is directed not toward state-of-the-art vibrational analyses akin to these but instead to providing a uniform and trustworthy comparison of 55 related molecules using scaled harmonic vibrational wavenumber values from DFT calculations. Experimental and calculated DFT wavenumber values for benchmark and target molecules are summarized in Tables 1−3. With a few exceptions, vibrational wavenumber values predicted with the 6-311+G(d,p) and aug-cc-pVTZ basis sets were within 15 cm^{-1} of each other and the former are not listed. Molecules of the class OMX_3 and MX_3 (M = P, As, Sb; X = F, Cl, Br, I) are presented in Table 3, including B3LYP/3-21G** and MP2/3-21G** data because the larger basis sets do not extend to antimony and iodine. Selected stretch vibrations are presented, coinciding with those modes actually assigned in the IR studies of molecules OP−X etc. The symmetry group for each calculated molecular structure is listed, to clarify whether it is linear or bent, trans or cis etc. In NCSSCN only the C_2 conformer with τ(CSSC) = 89.5° is listed as it was

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TABLE 1: Experimental Gas Phase and Calculated (Unscaled) MP2 and DFT Wavenumber Values for Molecules with Questionable Vibrational Assignments

molecule	sym	mode	experiment/cm^{-1}	ref	valid?[a]	B3LYP[b]/cm^{-1}	IR intens/km·mol^{-1}	MP2[b]/cm^{-1}
OPCN	C_s	CN str	2165 s	4	√	2261	82	2073
		OP str	1385 m		X	1237	68	1169
		CP str				581	147	584
OPSCN	C_s (trans)	CN str	2055 m	5	X	2263	29	2099
		OP str	1365 s		X	1262	154	1208
		CS str	720 w		√	695	0.02	710
		PS str	680 w		X	499	81	501
	C_s (cis)	CN str				2264	11	2085
		OP str				1267	104	1205
		CS str				699	3	713
		PS str				440	5	434
NS−SCN	C_s (trans)	CN str	2060 s	9	X	2234	39	2063
		N═S str	1365 s		√	1344	86	1586
		CS str	712.6 m		√	707	0.01	729
	C_s (cis)	CN str				2232	15	2007
		N═S str				1339	84	1312
		CS str				716	0.01	828
NSCN	C_s	CN str	2224 m	8	?	2252	67	
		N═S str	1374 s		X	1233	13	
		CS str				532	71	
OCNCN	C_s	CN str	2280 s	33	?	2406	1446	
		CN str	2233.1 vs		?	2350	126	
		OC str	1429.4 s		?	1541	4	
		C−N str	1073.5 s		X	862	9	
		∠NCO (A′)				611	29	
		∠NCO (A″)				575	18	
		∠NCN (A′)				496	18	
		∠NCN (A″)				472	17	
		∠CNC (A′)				123	4	

[a] Checks, question marks, and X's indicate whether the agreement between observed IR bands and DFT predictions is acceptable, marginal, or poor. [b] aug-cc-pVTZ basis set.

preferred over the C_{2h} (i.e., trans planar) conformer by 18 kJ mol^{-1}, while the C_{2v} (i.e., cis planar) conformer is a saddle point and not a PE minimum. OPSCN and NSSCN data plotted in Figures 1−4 refer to planar trans conformers, although the planar cis conformers are also included in Table 1 and are discussed below.

Experimental vs calculated CN stretch frequencies are plotted in Figure 1. The benchmark data (open circles) include molecules with simple and cumulated CN groups, with 20 vibrations in the range 1900−2400 cm^{-1}. The line of best fit for the benchmark data points corresponds to a scaling factor of 0.9635, with an rms error of 17 cm^{-1}. Data for molecules with unproven vibrational assignments are also shown (solid diamonds). Two molecules definitely do not fit the trend: OPSCN and NSSCN. Marginal agreement is found for NSCN (the experimental value is 54 cm^{-1} higher than scaled prediction) and the two CN vibrations of OCNCN (experimental values 38 and 31 cm^{-1} lower than scaled predictions). The agreement for OPCN appears to be quite acceptable.

Figure 2 displays the relationship between experimental and calculated CS stretch vibrations. The benchmark data include four molecules containing an −SCN group for better comparison with OPSCN and NSSCN. The scaling factor derived from the 10 benchmark data points is 0.9849, with an rms error of 9 cm^{-1}. The NSSCN and OPSCN data points are close enough to the trend line (16 and 35 cm^{-1} respectively) that they cannot be ruled out. Very low calculated IR intensities, however, make observation of CS stretch bands in NSSCN and OPSCN unlikely.

The OP stretch data plotted in Figure 3 are for benchmark molecules incorporating OP bonds with more than single bond character. Their vibrations lie in the region 1200−1450 cm^{-1}. The scaling factor derived from the 10 bench mark data points is 1.0018, with an rms error of 16 cm^{-1}, although the data points in this region actually suggest a line of steeper slope with a nonzero origin. The experimental values assigned to OPCN and OPSCN exceed the scaled benchmark predictions by over 100 cm^{-1}, indicating they are extremely unlikely to be correct.

The scarcity of experimental data on molecules incorporating NS groups restricts the benchmark set to five molecules, but the range of observed wavenumber values is adequate for comparison with NSCN and NSSCN. A scaling factor of 0.9721 leads to an rms error of 8 cm^{-1}. As shown in Figure 4, the NSSCN and, in particular, the NSCN assignments show very poor agreement with the trend.

The ON stretch data presented in Figure 5 are for molecules incorporating an ON group with bond order greater than one. The strongly linear relationship (scale factor 0.9511, with rms error of 13 cm^{-1} for seven points) supports the assignments of ONCN and ONCCN modes. It also suggests that B3LYP/aug-cc-pVTZ performance should be adequate for OPCN, since its ONCN analogue is right on the trend line for both CN and ON stretch modes.

To investigate $OSbF_3$ and $OSbCl_3$, nine benchmark molecules incorporating OM, M−F, or M−Cl stretches vibrations (M = group V atom) were calculated using the 3-21G** basis set. Data on O═Sb double bonds are virtually nonexistent,[15] but the O═As stretch of $OAsCl_3$ and O═P stretches of OPX_3 (X = F, Cl, Br) may be used for comparison. B3LYP/3-21G** results for these stretch vibrations are within 3% of experimental values (Table 3), but MP2/3-21G** wavenumber values are too high, particularly for $OAsCl_3$. The O−Sb *single* bond stretch of H_2SbOH is overestimated by 8% and 11% respectively at the B3LYP and MP2 levels. In stark contrast to the benchmark

TABLE 2: Experimental and Calculated (Unscaled) DFT Wavenumber Values for Benchmark Molecules with Reliable Vibrational Assignments

molecule	sym	mode	experimental/cm^{-1}	phase	ref	B3LYP^a/cm^{-1}	IR intens/km·mol^{-1}
ONCN	C_s	CN str	2170	gas	35	2265	31
		ON str	1501			1588	107
		C−N str	820			820	53
		∠NCN	588.5			633	22
HCN	$C_{\infty v}$	CN str	2096.85	gas	29	2200	2
HOCN	C_s	CN str	2294	N_2	36	2374	134
		OC str	1098			1097	76
CNCN	$C_{\infty v}$	CN str	2302.001	gas	37	2387	118
		CN str	2059.731			2132	166
NCCN	$C_{\infty v}$	CN str	2330.5	gas	38	2429	0
		CN str	2157.83			2266	0.007
ClCN	$C_{\infty v}$	CN str	2215.6	gas	29	2308	45
HCCCN	$C_{\infty v}$	CN str	2273.996	gas	39	2367	25
OCN	$C_{\infty v}$	CN str	1921.28	gas	40	1978	74
		OC str	1266.63	gas		1296	9
ONCCN	$C_{\infty v}$	CN str	2356	Ar	41	2468	794
		CN str	2192	gas	42	2289	33
		ON str	1445	gas		1491	243
OCNH	C_s	CN str	2268.89	gas	43	2324	758
		OC str	1327			1335	0
OCNF	C_s	CN str	2174	Ar	44	2238	546
OCNCl	C_s	CN str	2212.2	gas	33	2269	914
		OC str	1306.6			1355	3
OCNBr	C_s	CN str	2198	gas	33	2261	1023
		OC str	1294.5			1350	7
OCNNCO	C_{2h}	CN str (b_u)	2208	gas	45	2269	2340
SCHCN	C_s	CN str	2221	Ar	46	2308	8
		CS str	1103			1123	37
Cl−SCN	C_s	CN str	2170	gas	33	2241	2
		CS str	678.9			690	6
Br−SCN	C_s	CN str	2145.1	gas	33	2239	2
		CS str	674.2			692	5
NCSSCN	C_2	CN str (b)	2158	gas	33	2260	2
		(a)				2255	1
		CS str (b)	671			681	5
		(a)				675	3
CS	$C_{\infty v}$	CS str	1271.162	gas	47	1305	86
OCS	$C_{\infty v}$	CS str	858.95	gas	29	873	10
		OC str	2062.22			2107	758
cyc-CS_2	C_{2v}	CS str (a_1)	881.3	N_2	48	888	21
		CS str (b_2)	520.9			508	94
CS_2	$C_{\infty v}$	CS str	1535.35	gas	29	1550	684
		CS str	657.98			674	0
OPF	C_s	OP str	1297.5372	gas	1	1301	98
		PF str	819.571	gas		789	185
		bend	416	Ar	49	404	21
OPCl	C_s	OP str	1263.007	gas	6	1277	115
		PCl str	489	Ar	50	479	163
		bend	308	Ar		297	4
OPBr	C_s	OP str	1257.844	gas	19	1272	135
		PBr str	407.1	Ar	51	403	118
		bend	253.7	Ar		244	3
OP	$C_{\infty v}$	OP str	1220.249	gas	52	1249	57
P_2O	$C_{\infty v}$	OP str	1277.645	gas	53	1285	155
PO_2	C_{2v}	OP str (b_2)	1327.53	gas	54	1299	93
OPF_2Cl	C_s	OP str	1358	gas	21	1362	190
NSF	C_s	NS str	1375.636	gas	55	1402	22
NSCl	C_s	NS str	1325	gas	38	1367	56
NSBr	C_s	NS str	1313	Ar	56	1356	77
NS	$C_{\infty v}$	NS str	1204.276	gas	57	1248	7
N_2S	$C_{\infty v}$	NS str	752	Ar	58	767	30
NO	$C_{\infty v}$	ON str	1876.0	gas	59	1968	43
FNO	C_s	ON str	1843.5	gas	38	1946	270
ClNO	C_s	ON str	1799.7	gas	38	1912	646
NO_2	C_{2v}	ON str	1617.8	gas	38	1688	437
		ON str	1318			1386	0

[a] aug-cc-pVTZ basis set.

molecules, the experimental bands assigned to O═Sb stretch vibrations of $OSbF_3$ and $OSbCl_3$ exceed the B3LYP and MP2 values by over 300 and 200 cm^{-1} respectively.

Antisymmetric M−Cl stretch vibrations (symmetry *E*) in $OPCl_3$, $AsCl_3$, $OAsCl_3$, and $SbCl_3$ are, on average, underestimated by 1% at the B3LYP level but are overestimated by an

TABLE 3: Experimental and Calculated (Unscaled) Wavenumber Values for $OSbF_3$, $OSbCl_3$, OPI_3, and Related Benchmark Molecules

molecule		experiment/cm^{-1}	ref	comment	MP2^a/cm^{-1}	B3LYP^a/km·mol^{-1}	IR intens/cm^{-1}	B3LYP^b
$OSbF_3$^{c}	OP str	*1272?*	10	X^d	1036.4	917.1	18	
	SbF str (E)	*946?*		X	773.9	748.3	90	
	SbF str (A_1)	*826?*		?	757.5	725	17	
$OSbCl_3$	OP str	*1217?*	10	X	1003.9	892.1	15	
	SbCl str (E)	*540?*		X	405	383.3	154	
OPF_3	OP str	1416.6	7	gas	1491.4	1449.1	186	1393.6
	PF str (E)	991.2			1079.4	1051.7	366	954.2
	PF str (A_1)	872			909.2	876	26	838.3
$OPCl_3$	OP str	1326	21	gas	1342.6	1321.3	108	1301.6
	PCl str (E)	590			610.5	572.3	499	559.0
$OPBr_3$	OP str	1297.9	7	gas	1322.4	1300.5	91	1280.0
	PBr str (E)	490			527	506.1	394	464.0
OPI_3	OP str	*1285?*	7	?	1295.4	1274.1	67	
	PI str (E)	*426?*			423.6	406.7	329	
$OAsCl_3$	OAs str	987	23	gas (Raman)	1101.9	1016.9	35	1002.6
	AsCl str (E)	441			457.7	431.6	227	412.2
	AsCl str (A_1)	412			438.2	408.8	18	388.9
	Δ^{18}OAs str	-45	25	Kr	-51	-46.9		-46.7
AsF_3	AsF str (A_1)	738.5	22	N_2	814	777.33	45	712.3
	AsF str (E)	698.8			805.6	767.4	142	674.1
$AsCl_3$	AsCl str (A_1)	416.5	22	gas	445.6	422.2	25	401.9
	AsCl str (E)	391			427.7	399.2	197	372.7
SbF_3	SbF str (A_1)	654	22	N_2	750.4	723.2	34	
	SbF str (E)	624			746.49	720.7	96	
$SbCl_3$	SbCl str (A_1)	380.7	22	gas	391.3	367.8	27	
	SbCl str (E)	358.9			379.2	355.7	155	
H_2SbOH	O−Sb str	583.5	24	Ar	648.9	628.9	100	

[a] 3-21G** basis set. [b] aug-cc-pVTZ basis set. [c] All molecules in this table possess C_{3v} symmetry, except H_2SBOH (C_s). [d] Question marks and crosses indicate marginal and poor agreement, respectively, between observed IR bands and DFT predictions.

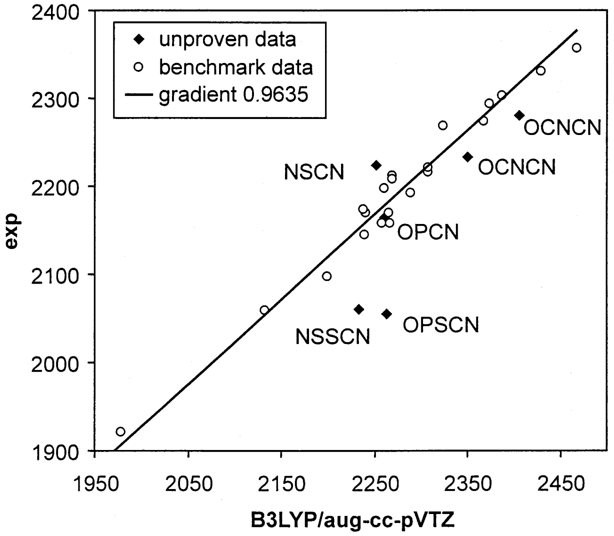

Figure 1. Experimental vs calculated wavenumber values for CN stretch vibrations, based on data in Tables 1 (unproven) and 2 (benchmark).

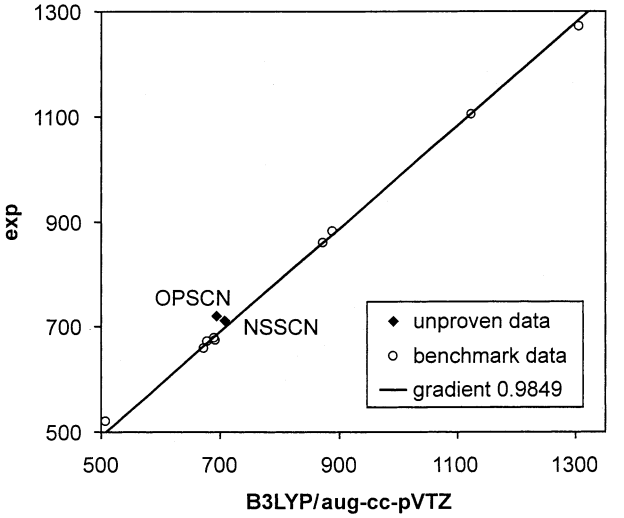

Figure 2. Experimental vs calculated wavenumber values for CS stretch vibrations, based on data in Tables 1 (unproven) and 2 (benchmark).

average of 6% at the MP2 level. The corresponding M−F stretch vibrations in OPF_3, AsF_3, and SbF_3 are overestimated by 6−15% at the B3LYP level and by 9−20% at the MP2 level. Calculated vibrational wavenumber values for Sb−F and Sb−Cl stretch vibrations in $OSbF_3$ and $OSbCl_3$, however, are much lower than the experimental values. The differences amount to 198 and 157 cm^{-1} at the B3LYP level, suggesting that the experimental assignments are most likely in error.

Molecules with unproven vibrational assignments are listed in Table 1 or the top of Table 3. Checks, question marks, and X's in these tables indicate whether the agreement between observed IR bands and DFT predictions is acceptable, marginal, or poor. OPCN, OPSCN, NSCN, NSSCN, OCNCN, $OSbF_3$, and $OSbCl_3$ all have at least one assignment which is not consistent with the DFT data. These, and other OP−X molecules are examined further below.

4. Discussion

4.1. OPCl. The key to several pyrolytic syntheses (OPF, OPBr, OPCN, OPSCN)[2−5] was initial generation of OPCl. To investigate whether the low resolution (4 cm^{-1}) spectrum reported in these publications is indeed OPCl, the contour of the OP stretch band was simulated using accurate rotational and centrifugal distortion constants of OP^{35}Cl from the work of Bell et al.[6] Spectral line position and intensities were generated with the SPFIT/SPCAT programs of Pickett,[16] assuming a temper-

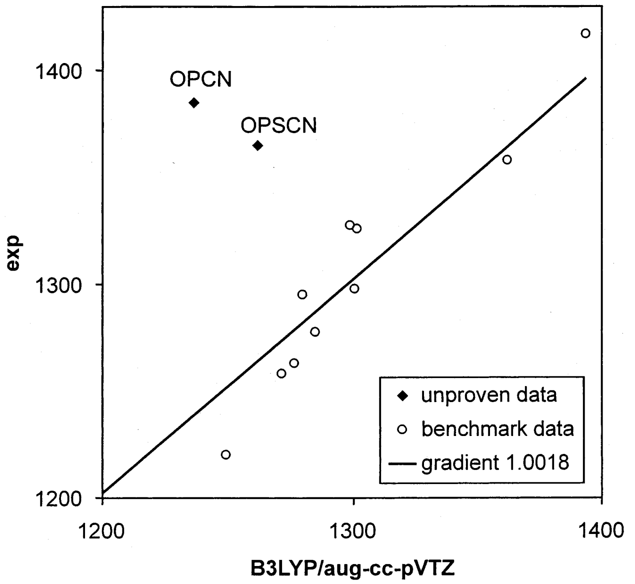

Figure 3. Experimental vs calculated wavenumber values for OP stretch vibrations, based on data in Tables 1 (unproven) and 2 (benchmark).

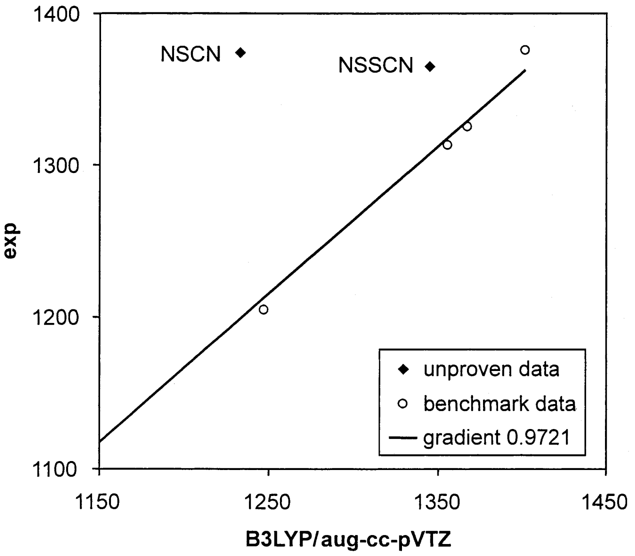

Figure 4. Experimental vs calculated wavenumber values for NS stretch vibrations, based on data in Tables 1 (unproven) and 2 (benchmark).

ature of 410 K in keeping with the cell temperature quoted in ref 2 (140 °C). A Gaussian line shape of fwhm 4 cm^{-1} was applied to generate the simulated contours, shown in Figure 6. The A′ symmetry of the OP stretch mode allows a-type or b-type rovibrational transitions, although Bell et al. found that a-type lines predominate.[6] Clearly, neither the a-type nor the b-type simulations of Figure 6 correspond to the experimental spectrum. Including the OP^{37}Cl isotopomer in the simulations would not help the comparison as its band center is slightly shifted to lower wavenumber (−0.004 cm^{-1} at the B3LYP/aug-cc-pVTZ level). The PR separation of the a-type simulation in Figure 6, based on measured rotational constants, is 20.0 cm^{-1}. The calculated value of just 10.1 cm^{-1} quoted in ref 2 suggests poor assumptions concerning the assumed molecular geometry.

The 492 cm^{-1} band that Allaf and Boustani assign to the PCl stretch vibration of OPCl is even more narrow than the 1273 cm^{-1} band [2] and cannot be reconciled with the simulated band-shapes either. In conclusion, the spectra given in refs 2−5 do not show OPCl as claimed.

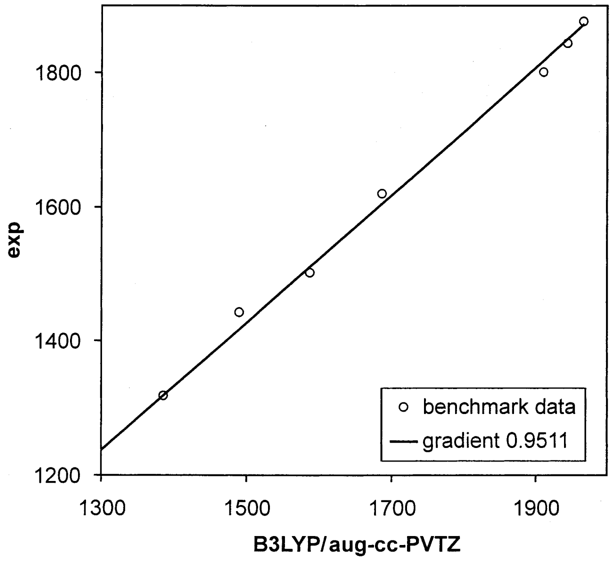

Figure 5. Experimental vs calculated wavenumber values for NO stretch vibrations, based on data in Table 2.

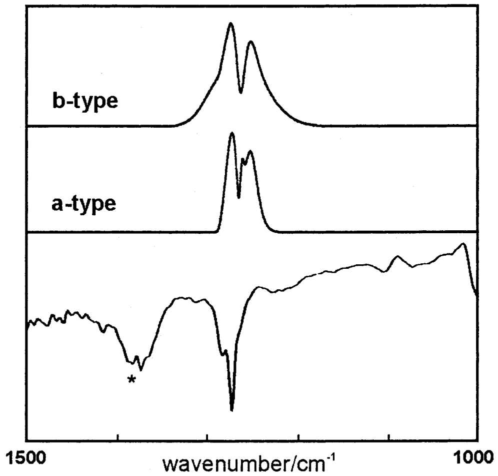

Figure 6. Simulated contours of the OPCl ν_1 band at 410 K, with the low resolution (4 cm^{-1}) experimental transmittance spectrum reported as OPCl (adapted from Figure 3 of ref 2) shown below. The feature marked $*$ was erroneously assigned to OPF. Spectral line position and intensities were generated with the SPFIT and SPCAT programs,[16] and a Gaussian line shape of fwhm 4 cm^{-1} was subsequently applied.

We note also that the precursor spectrum of Figure 2 in ref 2 is not that of OPCl$_3$, as claimed. This was pointed out earlier by Paplewski et al., who suggested that the molecule might be hexamethyldisiloxane resulting from degradation of the silicone grease.[17] The observed IR spectrum, however, exactly matches octamethylcyclotetrasiloxane.[18] This compound, a major component of silicone vacuum grease, is sufficiently volatile (mp 17 °C; bp 173 °C) that it may be observed in a heated cell.

4.2. OPBr. In a recent IR laser diode study, rovibrational analysis provides conclusive evidence for observation of OPBr, with OP stretch band origins of OP^{79}Br and OP^{81}Br reported at 1257.844 and 1257.818 cm^{-1}.[19] The value reported by Boustani and Allaf is 1268 cm^{-1},[3] a discrepancy of 10 cm^{-1}. The explanation is straightforward. The three strongest peaks in their low resolution IR spectrum, including that at 1268 cm^{-1}, are octamethylcyclotetrasiloxane.[18]

4.3. OPI$_3$. In Allaf's IR study on phosphoryl halides,[7] OPI$_3$ appears conspicuous as the odd one out. The *positions* of bands

TABLE 4: Observed and Calculated PR Separations for O═P and O═Sb Stretch Bands

molecule	geometry B3LYP	shape	A/cm^{-1}	C/cm^{-1}	temp/K	calcd PR sep^{a}/cm^{-1}	obsd PR sep^{b}/cm^{-1}
OPF_3	aug-cc-pVTZ	oblate	0.15603	0.14871	298	22.1	23.5
$OPCl_3$	aug-cc-pVTZ	prolate	0.06479	0.04727	298	15.1	15.0
$OSbF_3$	3-21G**	oblate	0.11227	0.09455	423	20.7	19.0
$OSbCl_3$	3-21G**	prolate	0.04488	0.03676	423	14.8	22.5

[a] Calculations performed using eq 1 of ref 26. [b] Observed PR separations were remeasured from figures in refs 2 and 10, as some of the tabulated values in those papers are not consistent with the corresponding spectrum.

assigned to OPI_3 are consistent with the general trend (and with the DFT predictions of Table 3), but the band shapes and intensities are not. The first three spectra in the series, OPF_3, $OPCl_3$, and $OPBr_3$, are undoubtedly correct as they are known from previous matrix and gas-phase work.[20,21] Their OP and PX stretch bands show a consistent decrease in width associated with increasing moments of inertia. The band assigned to the OP stretch of OPI_3, however, is broad, and there is no sign of the Q-branch evident in the other halides. Strangely enough, the possible reason given for both these observations in ref 7 is “decreases in electronegativity from fluorine up to iodine”. The second band assigned to OPI_3, found at 426 cm^{-1}, is much weaker. Again, this contrasts with the trend seen in OPF_3, $OPCl_3$, and $OPBr_3$ where the antisymmetric PX stretch bands are considerably stronger than the OP stretch bands. The ratios of OP to PX stretch intensities calculated at the B3LYP/3-21G** level are 0.51, 0.22, 0.23, and 0.20 for the OPF_3, $OPCl_3$, $OPBr_3$, and OPI_3 compounds; see Table 3. The first three are in good qualitative agreement with observation, and the ratio for phosphoryl iodide suggests that its band intensities should closely follow the pattern seen in $OPCl_3$ and $OPBr_3$. In summary, the reported spectrum of OPI_3 is not at all consistent with the other phosphoryl halides.

4.4. OPI. The broad spectral band attributed to the OP stretch of OPI_3 [7] was displayed again in the study of OPI.[3] The shoulder feature at 1253 cm^{-1}, originally described as the P-branch of the OPI_3 band, is now assigned to the OP stretch of OPI. Yet the profiles in the 1200−1300 cm^{-1} region are virtually identical, which would imply that OPI and the molecule responsible for the adjacent feature are formed in exactly the same ratio from two completely different syntheses. The first reaction involved passage of $OPCl_3$ over KI, while the reported production of OPI relied on flowing OPBr over heated KI. Since the IR spectrum shows that the purported OPBr is actually silicone vacuum grease, the second synthesis can be discounted.

4.5. $OSbF_3$ and $OSbCl_3$. In Allaf’s study of antimony oxide trihalides, gas-phase IR bands are assigned to $OSbCl_3$ (1217, 540 cm^{-1}) and $OSbF_3$ (1272, 946, 826 cm^{-1}).[10] Our DFT (and MP2) calculations on these molecules indicate vibrational wavenumber values which are a great deal lower and clearly inconsistent with these assignments; see Table 3. Equivalent calculations with the 3-21G** basis set on OMX_3 and MX_3 benchmark molecules (M = group V atom; X = halide atom) show good agreement with experiment, so it seems unlikely that $OSbCl_3$ and $OSbF_3$ should be so poorly predicted.

The experimental assignments of antimony oxide trihalides are also undermined by comparison with related molecules. For example, the antisymmetric Sb−Cl stretch of $SbCl_3$ is found at 359 cm^{-1}.[22] Given that the corresponding As−Cl stretch vibrations of $OAsCl_3$ and $AsCl_3$ differ by just 50 cm^{-1} [22,23] the Sb−Cl stretch of $OSbCl_3$ might be expected around 410 cm^{-1}, rather than 540 cm^{-1}. The single bond O−Sb stretch of H_2-Sb−OH has been reported at 583.5 cm^{-1},[24] so a double bond O═Sb stretch mode exceeding 1200 cm^{-1} would be very surprising. Also, the apparent trend in O═M stretch vibrations as the group V atom increases is contradictory: $OPCl_3$ (1326 cm^{-1}), $OAsCl_3$ (987 cm^{-1}), $OSbCl_3$ (1217 cm^{-1}). Allaf and Ajji cast doubt on the assignment of the 987 cm^{-1} band, incorrectly describing it as very weak and suggesting that it may be a combination band ($2\nu_2 + \nu_6$) instead.[10] A revised assignment along these lines is unlikely as it would require the combination band to have medium strength IR and Raman bands, and the O═As stretch bands to be too weak for observation in either IR or Raman spectra. In any case, the −45 cm^{-1} isotopic shift of this band on ^{18}O substitution[25] is fully consistent with the O═As stretch mode (B3LYP/aug-cc-pVTZ, −47 cm^{-1}), but not the combination (B3LYP/aug-cc-pVTZ, −3 cm^{-1}).

Finally, we note that the observed PR separation of the 1217 cm^{-1} “$OSbCl_3$” band in Figure 2 of ref 10 (22.5 cm^{-1}) is considerably greater than in the corresponding $OPCl_3$ band (15.0 cm^{-1}). Values predicted by the method of Paul and Dijkstra[26] using DFT geometries are listed in Table 4. They indicate that the PR separation of the $OSbCl_3$ band at 150 °C is no greater than that of $OPCl_3$ at room temperature. All the evidence suggests that the observed IR bands are not those of $OSbCl_3$ and $OSbF_3$ as claimed.

4.6. NSCN. In ref 8, observed IR bands at 2224 and 1374 cm^{-1} [60] are assigned to the CN and NS stretch modes of NSCN. The DFT calculation on NSCN shows that the CN stretch position is in marginal agreement with the benchmark data (Figure 1), while the NS stretch position is clearly inconsistent with it (Figure 2). Comparison with literature spectra of other molecules yields a straightforward explanation. These observed bands actually belong to pyrolysis byproducts N_2O and SO_2[27]—their position and shape match precisely.

4.7. NSSCN. In the IR study of NSSCN,[9] only the planar trans conformer was mentioned. Our DFT calculations found a second planar conformer with cis arrangement about the SS bond. At the B3LYP/aug-cc-pVTZ level, the trans form is preferred by just 2.2 kJ mol^{-1} including zero point corrections. Calculated values in Figures 1, 2, 4 are for the trans conformer, although conformational differences in the three critical vibrations (CN, NS, CS stretches) are less than 8 cm^{-1}. Calculations were also carried out at the MP2 level of theory, and a quite different picture emerges. The MP2/aug-cc-pVTZ potential energy of the *cis*-NSSCN is 15.3 kJ mol^{-1} lower than the trans conformer or 13.0 kJ mol^{-1} if the zero point correction is included. The terminal nitrogen atoms of the cis conformer are separated by 3.55 Å at the B3LYP/aug-cc-pVTZ level, but at the MP2/aug-cc-pVTZ level, this reduces to 2.15 Å. By comparison, the experimental N···N separation in the NO dimer is 2.237 Å.[28] Significant conformational shifts in the CN, NS and CS stretch vibrations are found at the MP2/aug-cc-pVTZ level, for example $\bar{\nu}_{CN}(\text{cis}) = 2007$ cm^{-1} and $\bar{\nu}_{CN}(\text{trans}) = 2063$ cm^{-1}. Although experimental band assignments for NSSCN are not consistent with DFT vibrational predictions (Figures 1 and 4), they cannot be ruled out in the light of MP2 results on *cis*-NSSCN. Inspection of the experimental spectrum, however, reveals that the “NSSCN” bands at 2060, 1365, and 712.6 cm^{-1} are actually associated with OCS, SO$_2$, [27] and HCN[29] respectively. It is surprising that the stronger 1365 cm^{-1} band was not recognized since a weaker band of SO$_2$ at 1151 cm^{-1} was also observed and correctly assigned. Other prominent bands seen at 1535 and 2185 cm^{-1}, incorrectly assigned to (SCN)$_2$ and ClSCN, are actually CS$_2$.[27]

4.8. OPSCN. Our ab initio calculations show that OPSCN, like NSSCN, has planar trans and cis conformers. In contrast to NSSCN, however, MP2 and B3LYP calculations agree concerning the structure of *cis*-OPSCN and its stability relative to *trans*-OPSCN. The distances between terminal oxygen and nitrogen atoms in *cis*-OPSCN are 3.61 Å at the B3LYP level and 3.36 Å at the MP2 level. The potential energy differences relative to *trans*-OPSCN are +8.2 and +5.9 kJ mol^{-1} respectively (including zero point correction), so *cis*-OPSCN might be expected to make little contribution to the IR spectrum. In any case, conformational differences in the CN, OP, and CS stretches are less than 14 cm^{-1} at both levels of theory.

The experimental OPSCN work relied on reaction of OPCl with AgSCN.[5] The IR spectrum of pyrolysis products includes bands at 2055, 1365, 720, and 680 cm^{-1} that were assigned to CN, OP, CS, and PS stretches of OPSCN. It is evident from Figures 1 and 3 that the DFT predictions for CN and OP stretches are not in accord with these experimental wavenumber values. Also, the B3LYP value for the PS stretch vibration (499 cm^{-1}; see Table 1) is well below the observed band center (680 cm^{-1}). The authors of ref 5 refer to the P=S stretch band of ClPS at 716 cm^{-1} [30] as justification for this assignment, but direct comparison of single and double bond stretch frequencies is hardly appropriate. The S−P stretch vibration of H$_2$PSH (484 cm^{-1})[31] would serve as a better guide. The IR spectrum in ref 5 suggests a chemical cocktail, but reassignment of some “OPSCN” modes is possible. The shoulder band with PR type structure near 2055 cm^{-1} is almost certainly OCS, as was the case with NSSCN, and the 1365 cm^{-1} band is probably SO$_2$. Water and CS$_2$ are among the other observed impurities. In brief, there is no evidence for the presence of OPSCN.

4.9. OPCN. The IR study of OPCN also relied on initial generation of OPCl.[4] The authors describe bands resulting from pyrolysis at 2165, 1385, 963, and 730 cm^{-1}, with the first two ascribed to CN and OP stretch vibrations of OPCN. The 2165 cm^{-1} value may be a typographical error, however, as the high wavenumber band in Figure 3 of ref 4 is found at ca. 2105 cm^{-1}. DFT data on CN stretch vibrations lead to a prediction of 2178 cm^{-1} in good agreement with 2165 cm^{-1}, but not 2105 cm^{-1}. In any case, the OP stretch assignment is 146 cm^{-1} higher than may be expected from DFT data (see Figure 3) and quite incompatible with it. There is no reason to doubt the DFT calculation of OPCN, as the calculated vs experimental OP stretches of the benchmark molecules show a very consistent trend. Also, B3LYP/aug-cc-pVTZ vibrational predictions of analogue ONCN are excellent, and its NO stretch vibration lies right on the trendline (Figure 5). The MP2/aug-cc-pVTZ structure of OPCN (r_{OP} = 1.497 Å; α_{OPC} = 105.5°) is very similar to the B3LYP one (r_{OP} = 1.482 Å; α_{OPC} = 106.0°), and the unscaled OP stretch vibration of 1169 cm^{-1} is even further from the observed 1385 cm^{-1} band. The absence of any band in the region 1150−1250 cm^{-1} suggests that OPCN is not observed.

4.10. OCNCN. Cyanogen isocyanate (OCNCN) was initially selected as a benchmark molecule with cumulated CN stretch vibrations for comparison with OPCN, OPSCN, NSCN and NSSCN. Deviation of CN stretch vibrations from the expected DFT trend provided a reason to reexamine its IR spectrum. The two gas-phase IR studies of OCNCN involved passage of ClCN [32] or halogens[33] over heated AgNCO. The resultant spectra differed somewhat, with additional bands present in Mayer’s work as shown in Figure 7. The DFT stick spectrum is a very poor match to Devore’s experimental spectrum in several regards. The relative intensity of CN stretch modes appear to be switched, and the appearance of three strong features in the 1000−1800 cm^{-1} region cannot be readily explained. Devore’s assignment of the 1065 cm^{-1} band to an OCNCN fundamental is almost certainly incorrect. Mayer’s data suggest the presence of at least one more chemical species, with additional strong IR bands at 2330, 2278, 610, and 455 cm^{-1}. In a partial revision of Mayer’s findings, we suggest tentative assignment of these bands to OCNCN fundamentals since they are consistent with the DFT stick spectrum and microwave data do confirm that OCNCN can be produced by heating AgNCO.[34]

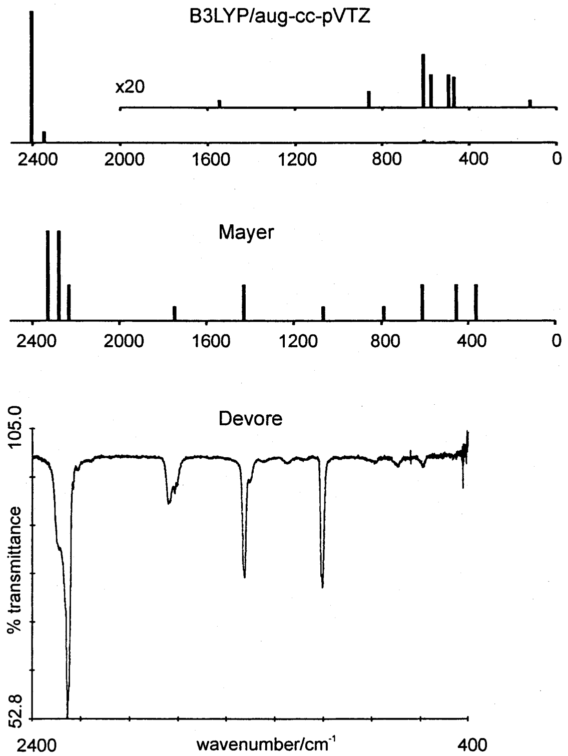

Figure 7. IR spectra of OCNCN. Top: Stick spectrum based on unscaled B3LYP/aug-cc-PVTZ data. Middle: Stick spectrum based on the tabulated gas-phase IR data of Mayer.[32] The three peak heights indicate whether bands were described as very strong, strong or medium (weak bands excluded). Bottom: Spectrum measured by Devore, adapted from Figure 7 of ref 33.

5. Conclusions

DFT-calculated vibrational modes, appropriately scaled with known vibrational data, together with a reexamination of the original spectral data in a systematic manner lead to revision of OCNCN assignments and the complete rejection of earlier low resolution vibrational assignments for OPI,[3] OPI$_3$,[7] OSbF$_3$, OSbCl$_3$,[10] OPCN,[4] OPSCN,[5] NSCN,[8] and NSSCN.[9] Conclusive, high-resolution IR studies from the groups of Bürger[1] and Davies[6,19] show that low resolution gas-phase assignments of OPF, OPCl,[2] and OPBr[3] were spurious also. There are a number of contributing reasons for the flawed assignments of these last 11 molecules and their inclusion in the literature. First, although in some cases ab initio calculations have been used to support the assignments, no scaling or comparison with calculations on similar molecules has been carried out. Second, the measuring and reporting of wavenumber values and spectral shapes and structures in the papers is sloppy and inadequate. In a number of cases, we have remeasured a number of band centers using the spectra provided in the papers to provide adequate values for comparison with theory and spectral prediction. Third, the limited use of spectral prediction and simulation of band shapes and PQR structure in the paper is flawed and misleading. In several cases, the observed band profiles were simply not consistent with the size of the molecule to which they were assigned. Observed and calculated PR separations were compared for bands of OPX, OPX_3 ($X = F$, Cl, Br, I), $OSbF_3$, and $OsbCl_3$, and the agreement was apparently excellent. This is most peculiar, however, given that seven of these 10 molecules were incorrectly assigned. The calculated separation for OPF_3, a molecule genuinely observed, conveniently matches the erroneous, tabulated experimental value of $43.1\ \mathrm{cm}^{-1}$. The actual separation, remeasured from the spectrum provided in ref 2, is closer to $23.5\ \mathrm{cm}^{-1}$. The rotational constants and temperature needed to repeat these calculations were not specified. Fourth, there is very little experimental detail in most of the papers to enable a reader to properly assess whether the spectra of the species postulated are likely to be observed under the conditions used. The procedure of heating the IR cell, which presumably was used in most of the experiments, is likely to produce artifacts, especially if an inappropriate silicone grease is used. Fifth, many of the spectra contained signals quickly attributable to a number of small molecules that often occur in pyrolysis systems, especially if the glassware is contaminated or there is a small vacuum leak.

Finally, low resolution IR spectroscopy by itself, while useful in assisting in the identification of pyrolysis products, does not provide unambiguous identification.

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Note Added in Proof. Recently, a further publication has appeared on the IR spectra of phosphorus trihalides (Zidan, M. D.; Allaf, A. W. *Spectrochim. Acta* **2002**, *58A*, 1577). Assignments of P−X stretching and umbrella modes in $SPBr_3$ and SPI_3 in this paper appear highly questionable in light of our ab initio calculations on these molecules. The calculations agree instead with the earlier findings of Nyquist,[21] which are not referenced in the new paper.

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