TABLE IV

PARTIAL MOLAL VOLUMES, CC. MOLE^{-1}, 25°

	H_2	D_2	A
n-C_7F_{16}	54(3)	54(4)	
c-$C_6F_{11}CF_3$			51(5)
i-C_8H_{16}			50(5)
c-$C_6H_{11}CH_3$			44(5)
CCl_4	38(H)		44(5)(2)
$C_6H_5CH_3$	36(4)(2)	35(3)	45(5)(3)(2)(3)
C_6H_6	35(4) 36(H)	34(3)	
CS_2			45(6)(6)
$CHBr_3$			44(4)

bons and i-C_8H_{18}. The increase is strikingly large in the case of H_2. It is evident, therefore, that the entropy of solution is mainly determined by the dilution, in terms of *mole fraction, not volume fraction*, necessary to balance the enthalpy. This confirms our recent findings for iodine dissolved in solvents of widely different molal volumes.[15]

We interpret the differences in volume and entropy between different gases and solvents as follows. We reiterate, first, a point all too easily forgotten, namely, that what we commonly designate as a partial molal quantity of the *solute* is in reality what takes place in the *system* when a differential amount of solute is added. In the case of solutions so dilute as those here considered, these changes represent what happens in the immediate neighborhood of the solute gas molecules. These have low attractive fields and small volumes but possess the same kinetic energy as the molecules of solvent, hence the latter gain added volume and freedom of motion, the greater the smaller their force fields, such as they would gain at the surface of a bubble. Although $\bar{V}_2$ is a little larger for argon than for hydrogen in CCl_4, this must be attributed mainly to its greater molecular size. Its volume per mole from its second virial coefficient is 49 cc., whereas that of hydrogen is 32 cc.[13] The solvent around a molecule of hydrogen approaches more nearly to the state of a bubble than that around a molecule of argon.

The force constants of the gases represented in Tables III and IV are much greater than the range in the solubility parameters of the solvents, hence the changes in entropy going horizontally in Table II, from one gas to another, are much larger than those going vertically, from solvent to solvent. The values of $\bar{V}_2$ for H_2 and D_2 in Table IV are so nearly the same as to fall within the experimental uncertainty, but they differ in the right direction to accord with the slight excess of entropy in the case of H_2.

This contribution to the entropy of solution accords also with the fact that, in going from gases with larger to those with smaller force constants, the entropy increases faster than ideal as given by $-R \ln x_2$. The lines in Fig. 3 have slopes of about -1.6 instead of -1.0.

We believe that these findings support an opinion often expressed by the senior author[16] that lattice models are not strictly appropriate for liquid solutions. A gas molecule is not oscillating in a cage with a definite frequency and then jumping to a new lattice site, but is rather participating with its solvent neighbors in a "random walk" with infinitesimal steps.

The relations revealed in the foregoing survey invite detailed theoretical study and reconciliation with our treatment of liquid-liquid solutions, but they are of such practical use and so suggestive as to model for theoretical treatment that we content ourselves provisionally with this presentation.

We express our gratitude to Dr. Berni J. Alder for helpful discussions during the course of this investigation, and to the Atomic Energy Commission for its support.

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(16) J. H. Hildebrand, *Disc. Faraday Soc.*, **15**, 9 (1953).

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Infrared Spectrum, Vibrational Assignment and Spectroscopic Entropy of Carbonyl Chloride[1]

BY EDWARD CATALANO AND KENNETH S. PITZER

RECEIVED SEPTEMBER 16, 1957

It had been believed, from correlation with fluorine and sulfur substituted analogs of carbonyl chloride, that the lowest frequency fundamental lay in the 220–240 cm.$^{-1}$ region. A search in the far infrared has failed to reveal the existence of this band. It is shown, by means of the "Matrix Isolation" method, that the gas phase 575 cm.$^{-1}$ band consists of two almost accidentally degenerate vibrational modes of different symmetry species. This leads to a new vibrational assignment with a calculated spectroscopic entropy which is almost in agreement with the calorimetric entropy, thus removing what has hitherto been regarded as a major third law discrepancy.

Introduction

The infrared and Raman spectra of phosgene have been investigated by a number of workers,[2-4] of which the Nielsen[4] work is the most recent and complete. In these investigations, only five of the six fundamentals were observed. These are at

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(1) This research was assisted by the American Petroleum Institute through Research Project 50.

(2) R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, **5A**, 285 (1937).

(3) C. R. Bailey and J. B. Hale, *Phil. Mag.*, **25**, 98 (1938).

(4) A. H. Nielsen, T. G. Burke, P. J. H. Woltz and E. A. Jones, *J. Chem. Phys.*, **20**, 596 (1952).

575, 1827, 297, 849 and 440 cm.$^{-1}$ for the gas phase infrared frequencies.[4] Polarization and intensity measurements for the Raman effect are known.[2] On the basis of a correlation with the spectrum of thiophosgene, Thompson[5] estimated the lowest fundamental to be at 230 cm.$^{-1}$. Nielsen[4] estimated 240 cm.$^{-1}$ from a correlation with fluorine substituted analogs of phosgene. (The existence of the vvw Raman band reported at 240 cm.$^{-1}$ is questionable.)

The calorimetric entropy has been determined by Giauque and Jones.[6] Giauque and Jones used the Thompson[5] assignment and the planar molecular structure of Brockway, Beach and Pauling[7] to calculate the spectroscopic entropy. They observed an apparent third law discrepancy of 1.6 cal./deg. mole at the boiling point. Zaslow, Atoji and Lipscomb[8] have looked into the X-ray crystallography of phosgene; they have concluded that there is no major disorder in the crystals at low temperatures.

We have searched the far infrared region for the predicted low frequency fundamental without success. The use of Nielsen's[4] data for F_2CO, FClCO and Cl_2CO (using 240 cm.$^{-1}$ for the predicted fundamental) for the application of the substitution product rule[9] indicated that possibly Nielsen's assignment was incorrect. The substitution product rule did indicate that an assignment with two bands of different symmetry species superposed at 575 cm.$^{-1}$ was reasonable. The results of the "Matrix Isolation" experiment demonstrated that this is the case.

The matrix isolation technique appears to be a valuable method for resolution of accidentally nearly degenerate bands.

Experimental

Commercial phosgene (Mathieson) supplied in a steel lecture bottle was dried with a 4 Å. molecular sieve (Linde), degassed and distilled under vacuum prior to use.

The Perkin–Elmer Model 21 was used for all experiments in the rocksalt region; the Model 12C was used in the KBr region. The far infrared gas phase work was performed with the grating instrument designed and constructed in this Laboratory.[10]

Infrared Gas Phase Measurements.—10 cm. glass cells with KBr windows with pressures up to 90 mm. of $COCl_2$ were used in the prism instrument range. Pressures up to 120 mm. and cell lengths of 0.7 and 2.8 m. were used in the far infrared (150–400 cm.$^{-1}$) region.

For the most part, the results of the gas phase measurements are identical with Nielsen's results. All the gas phase frequencies are listed in Table I. The lowest frequency fundamental was observed at 285 cm.$^{-1}$. This corresponds to Nielsen's 297 cm.$^{-1}$ band. We believe the 285 cm.$^{-1}$ value to be preferred since Nielsen's measurement was obtained with a KRS-5 prism spectrometer operating quite close to the cut-off frequency. We were not able to reduce the H_2O concentration to a low enough value to eliminate its pure rotational spectrum, but the H_2O did provide a wave length calibration[11] superposed on the $COCl_2$ band. We also note the appearance of a vvw band at 740 cm.$^{-1}$. Figure 1 shows the gas phase 575 cm.$^{-1}$ band.

TABLE I

ASSIGNMENT AND SYMMETRY OF OBSERVED INFRARED BANDS OF CARBONYL CHLORIDE IN GAS PHASE AND IN ARGON MATRIX AT 20°K.

Assignment	symmetry	Obsd. (cm.$^{-1}$) Gas phase	Obsd. (cm.$^{-1}$) Argon matrix	Calcd. (cm.$^{-1}$) Gas phase	Calcd. (cm.$^{-1}$) Argon matrix
ν_1	A_1	$(570)^a$	568^b		
ν_2	A_1	1827^c	1803		
ν_3	A_1	285	$(284)^d$		
ν_4	B_1	849^c	835		
ν_5	B_1	440^c	$(438)^d$		
ν_6	B_2	$(585)^a$	582		
$2\nu_3$	A_1	$..^e$	563	570	568
$\nu_3 + \nu_5$	B_1	740		725	
$\nu_1 + \nu_3$	A_1	$..^f$	808	855	852
$3\nu_3$	A_1			855	852
$\nu_1 + \nu_5$	B_1	1011^c	1006	1010	1006
$2\nu_1$	A_1	1159^c	1160	1140	1136
$2\nu_6$	A_1			1170	1164
$\nu_4 + \nu_5$	A_1	1276^c		1289	
$\nu_1 + \nu_4$	B_1	1412^c	1390	1419	1403
$\nu_5 + 2\nu_1$	B_1	1570^c		1580	
$\nu_5 + 2\nu_6$	B_1			1610	
$2\nu_4$	A_1	1677^c	1645	1698	1670
$\nu_1 + 2\nu_6$	A_1	$..^g$	1763	1740	1732
$\nu_1 + \nu_4 + \nu_5$	A_1	$..^g$	1835	1859	1841
$\nu_2 + \nu_3$	A_1	2130^c		2112	
$\nu_1 + \nu_2$	A_1	2405^c		2397	
$\nu_2 + 2\nu_5$	A_1	2705^c		2703	
$\nu_2 + 3\nu_1$	A_1	3527^c		2537	
$2\nu_2$	A_1	3636^c		3654	
$\nu_5 + 2\nu_2$	B_1	4073^c		4094	
?		4180^c			
$\nu_1 + 2\nu_2$	A_1	4255^c		4224	
$2\nu_2 + 2\nu_4$	A_1	5335^c		5352	
?		5408^c			

[a] Estimate from matrix data—see text. Center of gas phase band at 575 cm.$^{-1}$. [b] Average for isotope split band—see text. [c] Gas phase work of Nielsen and co-workers. See reference 4. [d] Estimate from gas phase data—see text. [e] This band would be masked by ν_1 and ν_6 in gas phase. [f] This band would be masked by ν_4 in gas phase. [g] This band would be masked by ν_2 in gas phase.

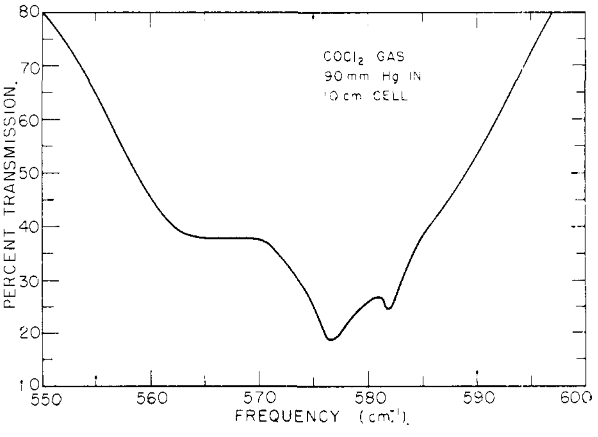

Fig. 1.

"Matrix Isolation" Experiment.—The "Matrix Isolation" technique in its various ramifications and applications to the study of reactive chemical species has been

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[5] H. W. Thompson, *Trans. Faraday Soc.*, **37**, 251 (1941).

[6] W. F. Giauque and W. M. Jones, THIS JOURNAL, **70**, 120 (1948).

[7] L. O. Brockway, J. Y. Beach and L. Pauling, *ibid.*, **57**, 2693 (1935).

[8] B. Zaslow, M. Atoji and W. N. Lipscomb, *Acta Cryst.*, **5**, 833 (1952).

[9] K. S. Pitzer and E. Gelles, *J. Chem. Phys.*, **21**, 855 (1953).

[10] C. R. Bohm, N. K. Freeman, W. D. Gwinn, J. L. Hollenberg and K. S. Pitzer, *ibid.*, **21**, 719 (1953).

[11] H. M. Randall, D. M. Dennison, N. Ginsburg and L. R. Weber, *Phys. Rev.*, **52**, 160 (1937).

described in detail by a number of workers.[12-15] Essentially, the technique consists of mixing or forming the species of interest with a transparent inert frozen material (matrix) at a very low temperature and looking at the species of interest spectroscopically. The matrix should provide a rigid cage around the species of interest, preventing contact between molecules being examined, diffusion of the species or free rotation. Thus, at the low temperature involved, vibrational frequencies appear as very sharp narrow bands.

It is found[13] that there is only a small frequency shift between the gas phase and the matrix; also, since the active molecules are well separated, there are no crystal splittings. These features are important for a study such as the present one.

We have used essentially the experimental technique detailed by Becker and Pimentel.[13] The matrix was purified argon. $A/COCl_2 = 820$. This mixture was deposited on a CsBr window maintained at 20°K. A total of 1.05×10^{-4} mole of $COCl_2$ was deposited. Figures 2 and 3 show the matrix phase spectra.

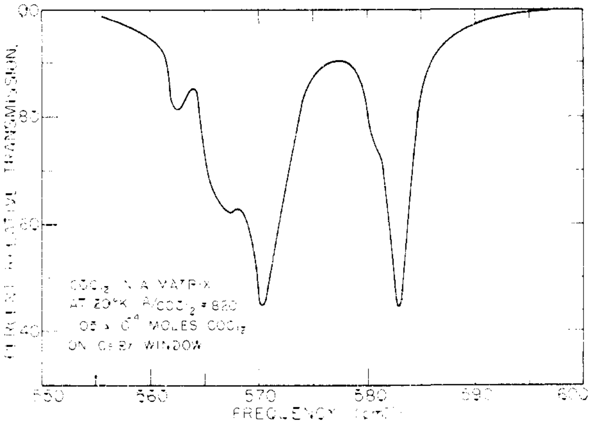

Fig. 2.

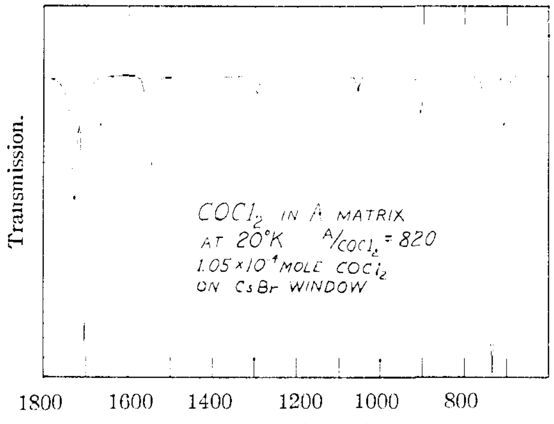

Fig. 3.

Discussion

Table I lists the observed gas and matrix phase bands for $COCl_2$ and our assignment (Herzberg's notation) for these bands.

It is apparent from Fig. 2 that the 575 cm.$^{-1}$ band consists of at least two separate vibrational bands of different symmetry species whose centers are at about 568 and 582 cm.$^{-1}$ in the matrix. The lower frequency band appears to have a large isotope splitting as compared to the higher frequency band. The intensity distribution for isotope splitting should be 9:6:1. The approximate experimental intensity ratio is (9):(6.6):(3.1), the lowest frequency component having about three times as much intensity as predicted. Also, if one takes the experimental shift in frequency for the $COCl^{35}Cl^{37}$ and $COCl^{35}Cl^{35}$ components, the shift between the assumed $COCl^{37}Cl^{37}$ and $COCl^{35}Cl^{37}$ components is too large. We therefore believe that the lowest frequency band at 563 cm.$^{-1}$ is primarily an overtone of the lowest frequency (ν_3) mode which has borrowed intensity from the ν_1 (568 cm.$^{-1}$) mode by resonance and that the $COCl^{37}Cl^{37}$ component of ν_1 must not have been resolved.

ν_1, ν_2 and ν_3 were chosen in the same manner as Nielsen[4] has done, using Raman intensity and polarization data.[2,4] That is, one of the 575 cm.$^{-1}$ bands must be ν_1; the other band must have B_1 or B_2 symmetry. The 849 cm.$^{-1}$ band must be B_1 symmetry (and therefore, ν_4) because of its intensity, location and unquestionable band contour.[4] The symmetry of the 440 cm.$^{-1}$ band is not as clearly demonstrable. Nielsen[4] assigns it as B_2 from his band contour. We have taken the 440 cm.$^{-1}$ band as B_1 symmetry (and ν_6 near 575 cm.$^{-1}$) since this assignment gives substitution product ratios which agree with the ratios for COF_2–$COFCl$ and for substituted methanes.[9] Using the Nielsen[4] assignment for COF_2, $COFCl$ and $COCl_2$ except as noted, the ratios are (substituting Cl for F in each case)

B_1 symmetry—one stretching and one bending motion in COX_2
- $r = 0.27$ for COF_2–$COCl_2$ (using 440 cm.$^{-1}$)
- $r = 0.35$ for COF_2–$COCl_2$ (using 575 cm.$^{-1}$)
- $r = 0.25$ for A′ in COF_2–$COFCl$
- $r = 0.22$–0.29 for substituted methanes[9]

B_2 symmetry—one bending motion in COX_2
- $r = 0.49$ for COF_2–$COCl_2$ (using 575 cm.$^{-1}$)
- $r = 0.41$ for COF_2–$COCl_2$ (using 440 cm.$^{-1}$)
- $r = 0.53$ for A″ in COF_2–$COFCl$
- $r = 0.49$–0.54 for substituted methanes[9]

We have chosen ν_1 to be the 568 cm.$^{-1}$ band since this band has a larger isotope splitting than the 583 cm.$^{-1}$ band and ν_1 would be expected to involve more Cl atom motion than ν_6. Therefore, 570 cm.$^{-1}$ (estimated gas phase frequency) is assigned to ν_1, 585 cm.$^{-1}$ to ν_6 and 440 cm.$^{-1}$ to ν_5.

The principal result of the matrix experiment, the splitting of the 575 cm.$^{-1}$ band, may also be explained as a Fermi resonance between ν_1 and $2\nu_3$. While we cannot claim to eliminate completely this interpretation, it is very difficult to account for the various details on this basis. Also one must assume that one low frequency fundamental has escaped detection even at a path length of 2.8 m. and 120 mm. of pressure. Thus we believe the assignment of separate fundamentals near 575 cm.$^{-1}$ to be correct.

A number of interesting features appeared in the matrix spectra that are not apparent from gas phase work. The matrix bands at 808, 1763 and 1835 cm.$^{-1}$ would have been masked in any of the gas phase investigations. The bands at 1763 and

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(12) E. Whittle, D. A. Dows and G. C. Pimentel, *J. Chem. Phys.*, **22**, 1943 (1954).

(13) E. Becker and G. C. Pimentel, *ibid.*, **25**, 224 (1956).

(14) H. P. Broida and J. R. Pellam, *Phys. Rev.*, **95**, 845 (1954).

(15) I. Norman and G. Porter, *Nature*, **174**, 508 (1954).

1835 cm.$^{-1}$ were assigned by rather complex combinations deriving intensity through resonance from the 1803 cm.$^{-1}$ fundamental. The 835 cm.$^{-1}$ matrix band has a shoulder on the high frequency side of the band whose origin remains obscure.

All band contours as observed by Nielsen, *et al.*,[4] agree with those predicted in the Table I assignment with the one exception of the 440 cm.$^{-1}$ band already mentioned.

The spectroscopic entropy has been calculated using the assignment in Table I and the microwave rotational constants of Robinson.[16]

At 280.66°K. (b.p.) S = 66.99 cal./deg. mole
298.16°K. S = 67.82 cal./deg. mole

This reduces the apparent third law discrepancy between calorimetric and spectroscopic entropy to 0.36 cal./deg. mole. In the calorimetric measurements,[6] an unusual expansion of the sample near the melting point stretched and eventually broke the resistance thermometer. There are also unresolved questions about the possible presence of a second crystalline form. Consequently the accuracy of the calorimetric entropy is questionable. Professor Giauque has told us of his intention to repeat the heat capacity measurements to firmly settle the third law value.

Acknowledgment.—We wish to thank Mr. Dolphus E. Milligan for aid in performing the matrix experiments.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Microwave Absorption and Molecular Structure in Liquids. XXI. Relaxation Times, Viscosities and Molecular Shapes of Substituted Pyridines, Quinolines and Naphthalenes[1,2]

BY ROBERT W. RAMPOLLA AND CHARLES P. SMYTH

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Dielectric constant and loss measurements at wave lengths of 1.25, 3.22 and 10.0 cm. and 300 m. have been carried out at 20, 40 and 60° on 1- and 2-methylnaphthalene, 1,2,3,4-tetrahydronaphthalene, 1-nitronaphthalene, 2-, 4-, 6- and 8-methylquinoline and 2,4- and 2,6-dimethylpyridine in the pure liquid state, and also on 1-nitronaphthalene in dilute benzene solution. These data have been used to construct arc plots from which were obtained the critical wave length, distribution coefficient and optical dielectric constant at each temperature. A change in the direction of the dipolar vector for similarly shaped, non-spherical molecules is found to have a marked effect on relaxation time but not on viscosity. A rough proportionality between relaxation time and viscosity is observed for molecules of not too different size and shape provided the direction of their dipolar vectors does not vary appreciably.

The investigation into the relations between dielectric relaxation and other molecular properties, such as size, shape and viscosity, has been extended to include a series of ten aromatic compounds, all but two of which are modifications of the basic naphthalene nucleus. The rigidity of the molecules eliminates some of the difficulties involved in the interpretation of these relations when internal rotation and bending are possible,[3,4] while the similarity in their sizes and shapes should afford a convenient basis for comparison. All the compounds have been measured in the pure liquid state, and, in addition, 1-nitronaphthalene has been investigated in dilute benzene solutions. The methods used in measuring the dielectric constants and losses of liquids and in calculating critical wave lengths have been described in previous papers of this series.[5-11]

Purification of Materials.—The 1,2,3,4-tetrahydronaphthalene and 4-methylquinoline used were obtained from Matheson, Coleman and Bell, Inc., the 6- and 8-methylquinoline from the Eastman Kodak Co., while the remaining six compounds were from Brothers Chemical Co. 2-Methylnaphthalene was fractionally crystallized at the melting point and distilled at reduced pressure. 1-Nitronaphthalene was fractionated at reduced pressure and recrystallized twice from heptane. The other compounds were refluxed over barium oxide for 24 hr. and then fractionally distilled. Analytical reagent grade benzene from the General Chemical Co. was used for the solution measurements without further purification. Although the boiling point of the 1-methylnaphthalene sample agreed well with the literature value, the fact that it was obtained from "Practical" grade material would seem to account for the anomalously high dipole moment value obtained for it in Table III. Boiling or melting points and refractive indices are tabulated below, together with values taken from the literature.

Experimental Results

The dielectric constants ϵ' and losses ϵ'', measured at 1.25, 3.22 and 10.0 cm., the static dielectric constants ϵ_0, measured at 300 m., the densities d and the viscosities η for the pure liquids are listed in Table I. Table II contains the slopes, a_0, a' and a'' of dielectric constant and loss against mole fraction for solutions of 1-nitronaphthalene in benzene. The data in Tables I and II have been used to construct Cole and Cole arc plots[12] from which critical wave lengths λ_m, distribution parameters α and infinite frequency or optical dielectric constants ϵ_∞ were obtained. The results at

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(1) This research has been supported in part by the Office of Naval Research. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

(2) This paper represents a part of the work submitted by Mr. R. W. Rampolla to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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