Infrared Studies of Matrix-isolated Species

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1 Introduction

Infrared spectroscopy has proved of considerable value in the structural determination of molecules. Its application to the study of matrix-isolated species has proved one of the most direct means of elucidating the structure of reactive molecules and studying their reactions. The matrix isolation technique involves the rapid cooling of a mixture of the absorbing substance (A) and a diluent gas (M) to form a solid matrix at a temperature sufficiently low to prevent diffusion and probable reaction of the reactive species (A). With high matrix : absorber ratios the solute may be expected to be 'isolated' in the solid matrix and the reactive species can be examined at will by i.r. and other structural techniques. The trapped species can be stable or unstable molecules, radicals or ions. The noble gases and nitrogen are ideally suited as matrices because of their inertness and i.r. inactivity, but other supports can also be utilised.

The term matrix isolation was introduced by Pimentel, who was the first to use the technique for the i.r. investigation of free radicals. A large proportion of the succeeding work has naturally been devoted to free radicals but many molecular species have also been studied in matrices. The combination of the two techniques offers a powerful approach to problems of molecular interactions between stable, as well as reactive, molecules. Under conditions of perfect isolation, the species under study is subject only to solute–matrix interactions. Such conditions are only achieved (and not necessarily so then) at very high matrix to solute (M : A) ratios. At low M : A ratios interactions between solute molecules become important; the method can thus be used to study solute–solute interactions which manifest themselves in the i.r. spectrum of the isolated dimeric or oligomeric species. These matrix disturbances influence the position, shape, and intensity of the solute absorption frequencies and, in principle, all of the effects are capable of yielding information concerning the intermolecular forces.

Several individual aspects of i.r. matrix studies have been reviewed, in particular, free radical species by Pimentel in Bass and Broida's text on 'The Formation and Trapping of Free Radicals';[1] by Jackson,[2] and by Jacox and Milligan;[3] and the isolation of high temperature species by Weltner.[4] A brief survey of ionic

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[1] A. M. Bass and H. P. Broida, eds., 'Formation and Trapping of Free Radicals', Academic Press, New York, 1960.

[2] J. L. Jackson, *J. Washington Acad. Sci.*, 1958, **48**, 181.

[3] M. E. Jacox and D. E. Milligan, *Appl. Optics*, 1964, **3**, 873.

[4] W. Weltner jun., Proceedings of the International Symposium on Condensation and Evaporation of Solids, 1962, 243.

and molecular species is given under the paragraph 'Solid Solutions' in Vedder and Hornig's review[5] of the i.r. spectra of crystals. Pimentel[6-8] has given brief general surveys of the early work and has also selectively reviewed the early data relating to frequency shifts and multiplet splittings. These latter and other matrix environmental effects have recently been reviewed by Hallam.[9]

The object of this article is to present a balanced perspective of this rapidly expanding area of research and to draw attention to the versatility and wide applicability of the matrix technique to stable as well as reactive species.

2 Experimental Procedures

A. Cryostat.—In principle, the experimental technique is simple: the solute and matrix molecules are suitably mixed using a conventional vacuum line system and then condensed on to an i.r.-transparent (*e.g.* alkali halide) plate which is an integral part of a low-temperature i.r. cell. In practice, the technique requires skill and careful control in the laying down of the solid matrix and demands a highly efficient cryostat. An excellent introduction to the experimental procedure has been given by Mauer in Chap. 5 of ref. 1 in which he describes several cryostats. They are all based on a double Dewar, an inner one for the primary refrigerant of liquid H_2 or He, and outer one of liquid N_2. These are now being replaced by miniature Joule–Thomson cryostats which employ built-in open-cycle liquefaction units, originally evolved to cool i.r. detectors in satellites.

Refrigeration is achieved by the open-cycle Joule–Thomson expansion of high pressure cylinder gases. Figure 1 shows the complete cryostat (developed by Air Products and Chemicals, Inc., and marketed under the trade name of Cryo-Tip) and matrix isolation cell. Essentially it comprises three units, the Dewar or vacuum shroud D (designed by White and Mann[10]), the liquefier L, and the matrix support window M. The liquefier consists of a heat exchanger which has two separate gas circuits, one for nitrogen and one for hydrogen. Each circuit consists of a pair of very fine capillary tubes wound round a mandrel, one connected to the high pressure gas inlet and the other to an outlet vent. High pressure gas, thus expanded by a throttling process, produces cooling provided it is originally below its inversion temperature. Nitrogen cools on expansion from room temperature so that in the operation of the Cryo-Tip high pressure nitrogen is expanded to produce liquid at 77°K, which cools the inflowing hydrogen gas below its inversion temperature. The cold hydrogen gas then undergoes expansion providing the final refrigeration at *ca.* 20°K at the tip. The base of L is sealed to allow a small pool of liquid hydrogen to collect; the exact low temperature achieved at the pool is a function of the gas pressure above it, *i.e.* the H_2 back pressure. To achieve temperatures higher than those normally

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[5] W. Vedder and D. F. Hornig, *Adv. Spectroscopy*, 1961, **2**, 189.
[6] G. C. Pimentel, *Spectrochim. Acta*, 1958, **12**, 94.
[7] G. C. Pimentel, *Pure Appl. Chem.*, 1962, **4**, 61.
[8] G. C. Pimentel and S. W. Charles, *Pure Appl. Chem.*, 1963, **7**, 111.
[9] H. E. Hallam in 'Molecular Spectroscopy', Proceedings of the 4th Institute of Petroleum Hydrocarbon Research Conference, 1968, 329, Institute of Petroleum, London.
[10] D. White and D. E. Mann, *Rev. Sci. Instr.*, 1963, **34**, 1370.

existing at the tip, the back pressure must be increased above atmospheric and, conversely, to obtain lower temperatures the back pressure must be lowered below atmospheric. The temperature can thus be easily varied from 16 to 200°K

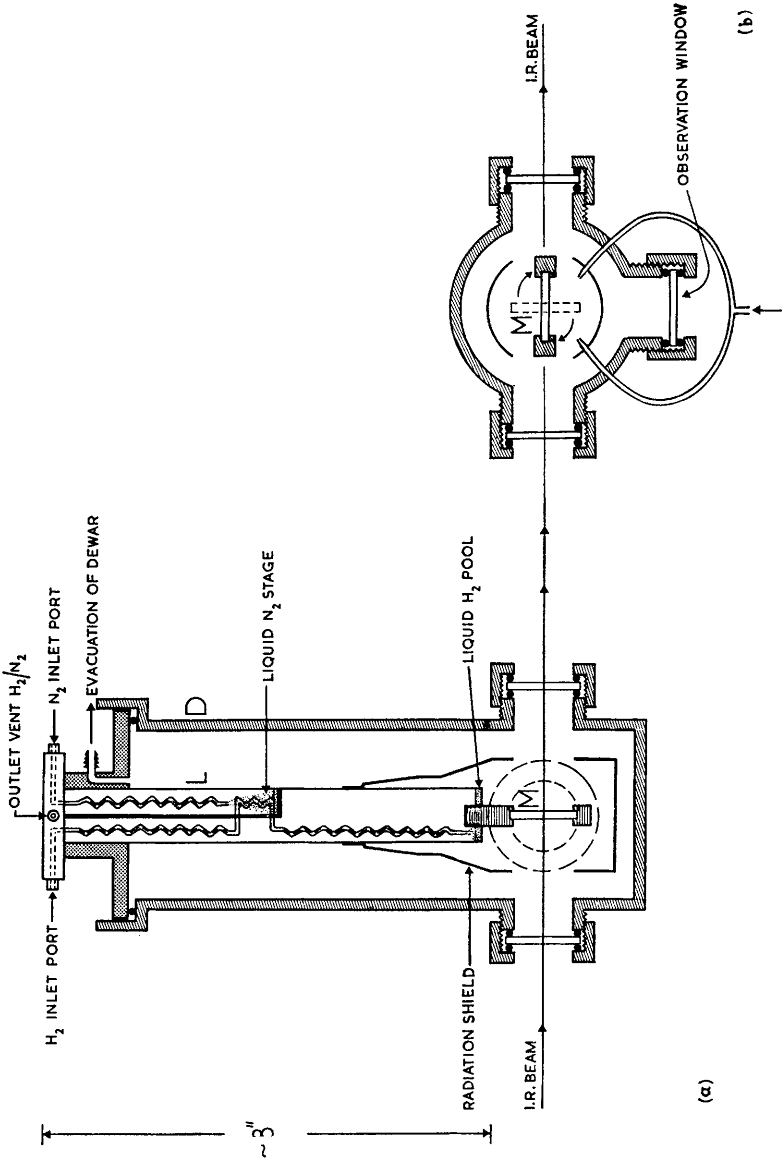

Figure 1 (a) *Miniature cryostat and matrix isolation cell*, D = *vacuum shroud*, L = *liquefier*, M = *matrix support window*; (b) *gas injection system*

and controlled to ±0·5°K or better by simply varying the H_2 exhaust pressure or the inlet H_2 and N_2 pressures. This feature represents a major advance in design compared with liquid refrigerant cryostats. A He–H_2–N_2 model is also available for the temperature range 4—300°K.

The matrix support window is mounted on the base of the liquefier and the whole assembly is supported on an O-ring flange to effect a vacuum seal to the Dewar. This permits rotation to align the matrix window either to the injection port(s) or to the optical windows. In a typical experiment, say with hydrogen chloride as a solute in an argon matrix, the solute and matrix gases are mixed in a vacuum line, by use of standard manometric procedures, in a suitable ratio (*ca.* 2000 for isolation of a strongly hydrogen bonding material in argon); the Cryo-Tip is evacuated and cooled down, with the refrigerant gases at their maximum pressures (*ca.* 45 min), and then the coolant gases are cut back to their working pressures; the mixture is sprayed onto the cold support window, at a rate of *ca.* 10 mmole h^{-1} to give a satisfactory matrix of argon, *via* a needle valve whilst pumping continuously on the cryostat to maintain a good vacuum—in this particular example, a deposition time of *ca.* 4 h would be required; then the spectrum is recorded and finally the system allowed to warm up to room temperature (*ca.* 3 h unless heat is supplied).

Closed-cycle miniature cryostats are also available which are based on the Stirling cycle (developed by Philips Laboratories and marketed by North American Philips Co. under the trade name of Cryogem). Refrigeration is achieved in a single space, simply by the out-of-phase operation of two pistons. The cycle begins (1) with compression (by an electric motor) of a gas at environmental temperature; next (2) the gas is transferred to a cold space, and passes through a cooler, which dissipates the heat of compression, a regenerator, which cools the gas nearly to the refrigerating temperature, and a freezer. Then (3) the gas is expanded into an expansion space, and becomes still cooler as a result of the work it does against the expansion piston. In phase (4) the piston moves the gas back to the compression space. On the way through the freezer the cold gas absorbs heat from whatever the machine is designed to cool, and then, passing through the regenerator, the gas picks up the stored heat and is returned to the environmental temperature for the commencement of a new cycle. These machines, which are extremely efficient, have a greater capital cost but are much lower in running costs.

B. Properties of Matrix Materials.—Most studies to date have aimed at keeping solute–matrix interactions to a minimum so that the materials most commonly employed for matrices have been the noble gases and nitrogen. Table 1 lists their pertinent physical properties together with those of some less inert molecules which occasionally have been used as matrices and whose use is expected to increase. It should be stressed that the technique is not restricted to these materials and current work indicates an increasing interest in more polar matrices.[11]

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[11] A. J. Barnes, H. E. Hallam, and G. F. Scrimshaw, *Trans. Faraday Soc.*, in the press.

Table 1 *Physical properties of matrix materials*

Matrix	*M.p.* (K)	*Lattice energy* (J mole^{-1})	*Thermal conductivity*[a] (W m^{-1}K^{-1})	*Subst. site diam.*[a] (Å)	*O_h int. site diam.*[a] (Å)
Ne	24·5	1874	4·4	3·155	1·31
Ar	84·0	7724	1·5	3·761	1·56
Kr	116·6	11,155	1·2	3·998	1·66
Xe	161·4	16,075	2·0	4·340	1·80
N_2	63·3	6904	0·4	4·00[b]	1·66[b]
O_2	54·4			3·64[b]	
CO	68·1	7950		4·00[b]	1·66[b]
N_2O	182·4	24,270		4·00[b]	1·66[b]
CO_2	(216·6)	27,000		3·93[b]	1·63[b]
CH_4	90·7		0·1	4·14	1·71
SF_6	(222·7)			5·01[c]	2·08[c]

[a] At 20°K, except Ne which is at 4°K; [b] Mean diameters; [c] Calculated assuming f.c.c. structure.

As in most other fields of solid-state chemistry it is essential that the matrix materials should be of a high degree of purity. Several non-reproducible spectra have been attributed to the presence of impurities in the lattice site, *e.g.* atmospheric N_2.

(i) *Diffusion.* Care must be taken to work at temperatures where the mobility of the trapped species is reduced to a minimum. The problem of diffusion in solid matrices has been discussed by Pimentel in Chap. 4 of ref. 1. In the absence of actual diffusion experiments on a system he gives the rough guide that the temperature required for a rigid matrix must be less than half the melting point, T_m, in °K, of the matrix. This guide is well known by investigators of solid state studies of non-stoicheiometric compounds as Tammann's rule, which relates the temperature, T_d, at which diffusion first becomes appreciable to the absolute m.p.: for salts, oxides, *etc.* $T_d \simeq 0{\cdot}57\, T_m$; for covalent compounds $T_d \simeq 0{\cdot}90\, T_m$. This is only a rough guide since clearly diffusion does not suddenly occur at a given temperature but gradually increases as the number of lattice defects increases and as progressively more solute molecules have sufficient thermal energy. Recent studies indicate that in some systems appreciable diffusion can occur below the Tammann temperature and it is therefore advisable always to operate at the lowest temperature attainable.

(ii) *Multiple trapping sites.* In a solid lattice there are several possible sites for trapped species, (*a*) substitutional sites, formed by the removal of a matrix molecule; (*b*) interstitial sites; and (*c*) dislocation sites. The noble gases Ne to Xe crystallise in f.c.c. lattices; so also does N_2 below 35°K and CO below 62°K. In an f.c.c. arrangement of spherical molecules a species trapped in a substitutional site will be equally surrounded by 12 matrix molecules. In such a lattice there are two different interstitial sites, a tetrahedral site formed by one spherical matrix molecule resting upon three other touching spheres, and an octahedral site formed by an arrangement of six spheres. An octahedral site is less than half the size of the surrounding spheres (Table 1) and could therefore entrap very small guest molecules; a tetrahedral site is less than one quarter the size of the matrix molecule and is unlikely to be a trapping site unless seriously distorted.

The intermolecular forces between matrix and absorber will differ for each site and the resulting perturbations of the energy levels may lead to two vibrational frequencies for a diatomic absorber, or two sets of frequencies for a polyatomic guest. Exceptionally careful studies are necessary to differentiate between molecular association, rotational, and multiple trapping site effects.

3 Applications

The matrix isolation method involves the spectroscopic examination of a species dispersed in a spectroscopically distinct host matrix. The trapped species can be molecules, radicals, or ions and many applications of each class have been reported. Guest ions when trapped in ionic matrices do not necessarily require cryogenic conditions, nor do clathrates (which have recently been reviewed by Child[12]). Although developed as a powerful technique for studying reactive species, the method is increasingly being employed for what are normally considered stable species. The reasons are that it enables the spectrum of essentially isolated molecules to be obtained, otherwise only attainable by the use of low-pressure gas studies in multi-reflexion cells employing total pathlengths of tens of metres. Furthermore, at low temperatures, the absorption bands are considerably narrowed which allows greater precision of measurement.

A. Molecular Association.—The method is ideally suited for hydrogen bonding studies. In the vapour phase it is difficult to follow the association of hydrogen bonding materials because of overlapping by the rotational structure; in condensed phases, the considerable bandwidth of the hydrogen bonded frequencies makes it virtually impossible to identify bands due to oligomers of definite size (*e.g.* Figure 2). Band breadths are also troublesome even in solution in non-polar solvents. For example, when examined at high concentrations in carbon tetrachloride, alkanols exhibit spectra in the 3 μm region approximating to those of the pure liquids, *i.e.* a broad absorption centred at *ca.* 3350 cm^{-1}. On progressive dilution this oligomer band gradually shows indications of a shoulder on the high frequency side which gives rise to a poorly defined dimer band at *ca.* 3500 cm^{-1} before the monomeric species becomes dominant. The breadth of the bands, however, makes it impossible to find bands due to oligomeric species intermediate between dimer and high polymer. The advantages afforded by matrix isolation to the study of such systems are enormous, controlled polymerisation allowing the identification of bands due to monomer, dimer, trimer, tetramer, and higher polymers, each of which gives comparatively narrow bands at the low temperatures used. Eventually, when a high degree of polymerisation is reached, bands analagous to the pure solid solute appear. This was elegantly

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[12] W. C. Child jun., *Quart. Rev.*, 1964, **18**, 321.

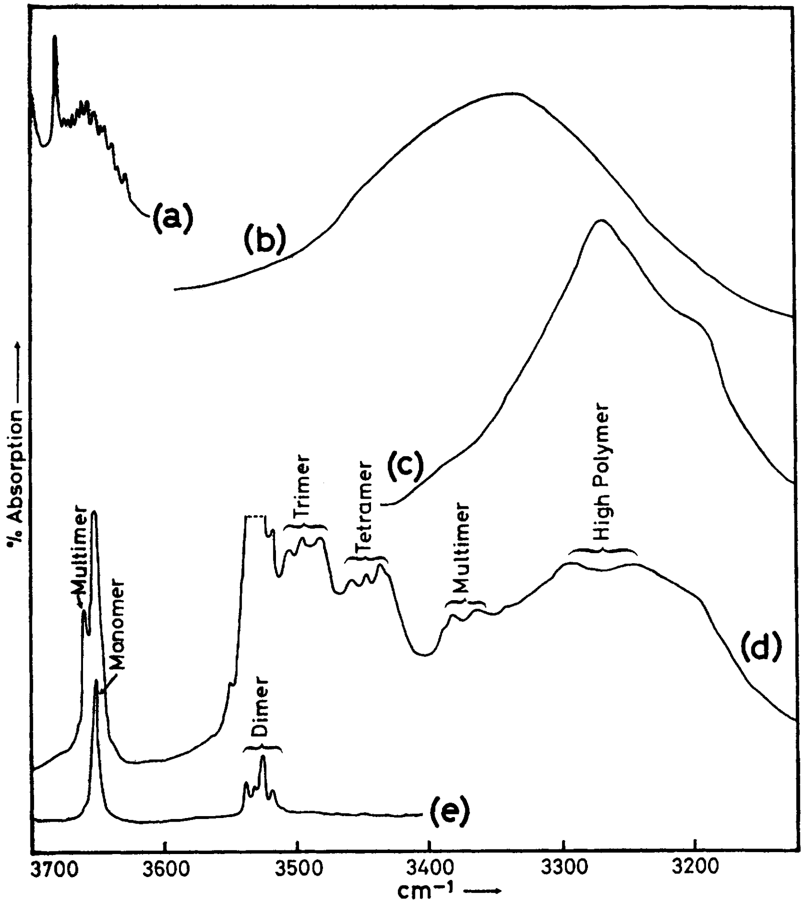

Figure 2 *I.r. spectra of methanol* OH *stretch* (a) *gas* (12 torr; 1 m); (b) *liquid* (*cap. film*); (c) *solid* (90°K); (d) Ar *matrix* (M/A = 20; 20°K); *the polymer band at* 3679 cm^{-1} *is due to the free* OH *of an open chain structure*; (e) Ar *matrix* (M/A = 1000; 20°K)

demonstrated in the early work of Pimentel's group on methanol,[13] water,[14] and ammonia[15] in nitrogen matrices.

These classic experiments were, however, intended only as a test of the efficiency of matrix isolation, with a view to its use in the free radical field, and the study of hydrogen bonding by this means has since been largely neglected. Some work has been done on the hydrogen halides,[11,16–18] hydrogen cyanide,[19]

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[13] M. van Thiel, E. D. Becker, and G. C. Pimentel, *J. Chem. Phys.*, 1957, **27**, 95.
[14] M. van Thiel, E. D. Becker, and G. C. Pimentel, *J. Chem. Phys.*, 1957, **27**, 486.
[15] G. C. Pimentel, M. O. Bulanin, and M. van Thiel, *J. Chem. Phys.*, 1962, **36**, 500.
[16] L. F. Keyser and G. W. Robinson, *J. Chem. Phys.*, 1966, **45**, 1694.
[17] M. T. Bowers and W. H. Flygare, *J. Mol. Spectroscopy*, 1966, **19**, 325.
[18] M. R. Atwood, M. Jean-Louis, and H. Vu, *J. Phys.*, 1967, **28**, 31.
[19] C. M. King and E. R. Nixon, *J. Chem. Phys.*, 1968, **48**, 1685.

and hydrazoic acid[20] in noble gas or nitrogen matrices, but a systematic investigation of hydrogen bonding materials in an inert matrix (such as argon) would obviously be of great value and offers considerable scope for further studies. Spectra of the OH stretching region of methanol in argon, from our recent work on alcohols,[21] are compared with the spectra of other phases in Figure 2. At the highest dilution the monomer OH stretching band at 3667 cm^{-1} is dominant but as the concentration is increased, bands due to dimer, trimer, tetramer, and high polymer (corresponding to pure solid methanol) successively grow in intensity. An identical pattern is also obtained for the OD stretching mode of CH_3OD. On the high frequency side of the monomer band a oligomer band is observed which must be due to the free $-OH(D)$ of an open-chain oligomer structure. The isolation of discrete oligomer species in an inert matrix appears to allow this absorption to be clearly differentiated since the feature does not appear in the spectrum taken in any other state (although a weak band close to, but on the lower frequency side of, the monomer band in solution has been tentatively ascribed to a terminal OH of a oligomer).

B. Molecular Rotation.—The rotational motion of trapped molecules has been widely studied. Assuming complete isolation in a noble gas matrix possessing a sufficiently large cavity, it might be expected that the rotational energy levels of small guest species would be only slightly perturbed. However, as a consequence of the low temperatures employed, only the low rotational levels will be appreciably populated. Thus for a diatomic molecule only the $R(1)$ $(J = 2 \leftarrow J = 1)$, $R(0)$ $(J = 1 \leftarrow J = 0)$, and $P(1)$ $(J = 1 \rightarrow J = 0)$ transitions would be expected to be observed in the vibration–rotation band, and the $J = 1 \leftarrow J = 0$ and $J = 2 \leftarrow J = 1$ transitions might be observed in the pure rotation region.

Evidence of rotational fine structure has been found for the fundamental vibrational frequencies of the hydrogen halides[22–27] water,[28–33] ammonia,[33,34] and methane[33,35–38] in noble gas matrices. For example HCl trapped in an argon matrix exhibits lines which correlate (Table 2) with the $R(1)$, $R(0)$, and $P(1)$

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[20] G. C. Pimentel, S. W. Charles, and K. Rosengren, *J. Chem. Phys.*, 1966, **44**, 3029.
[21] A. J. Barnes and H. E. Hallam, to be published.
[22] M. T. Bowers, G. I. Kerley, and W. H. Flygare, *J. Chem. Phys.*, 1966, **45**, 3399.
[23] L. J. Schoen, D. E. Mann, C. Knobler, and D. White, *J. Chem. Phys.*, 1962, **37**, 1146.
[24] M. T. Bowers and W. H. Flygare, *J. Chem. Phys.*, 1966, **44**, 1389.
[25] D. E. Mann, N. Acquista, and D. White, *J. Chem. Phys.*, 1966, **44**, 3453.
[26] J. M. P. J. Verstegen, H. Goldring, S. Kimel, and B. Katz, *J. Chem. Phys.*, 1966, **44**, 3216.
[27] L. F. Keyser and G. W. Robinson, *J. Chem. Phys.*, 1966, **44**, 3225.
[28] E. Catalano and D. E. Milligan, *J. Chem. Phys.*, 1959, **30**, 45.
[29] J. A. Glasel, *J. Chem. Phys.*, 1960, **33**, 252.
[30] T. Miyazawa, *Bull. Chem. Soc. Japan*, 1961, **34**, 202.
[31] R. L. Redington and D. E. Milligan, *J. Chem. Phys.*, 1962, **37**, 2162.
[32] R. L. Redington and D. E. Milligan, *J. Chem. Phys.*, 1963, **39**, 1276.
[33] H. P. Hopkins jun., R. F. Curl jun., and K. S. Pitzer, *J. Chem. Phys.*, 1968, **48**, 2959.
[34] D. E. Milligan, R. M. Hexter, and K. Dressler, *J. Chem. Phys.*, 1961, **34**, 1009.
[35] A. Cabana, G. B. Savitsky, and D. F. Hornig, *J. Chem. Phys.*, 1963, **39**, 2942.
[36] A. Cabana, A. Anderson, and R. Savoie, *J. Chem. Phys.*, 1965, **42**, 1122.
[37] F. H. Frayer and G. E. Ewing, *J. Chem. Phys.*, 1967, **46**, 1994.
[38] F. H. Frayer and G. E. Ewing, *J. Chem. Phys.*, 1968, **48**, 781.

Table 2 *Rotational features of* HCl *in gas,* Ar *matrix, and quinol clathrate*

Band	*Gas*	Ar *Matrix*	*Clathrate*
$J = 0 \rightarrow J = 1$	20·9	18·3	20
Translation		73	52
$v + v_{\text{trans}}$		2944	
$R(1)$ $^{35/37}$Cl	2925·4	2897	
$R(0)$ ^{35}Cl	2906·2	2888·2	
$R(0)$ ^{37}Cl	2904·1	2885·9	
$P(1)$ ^{35}Cl	2865·1	2854·2	
$P(1)$ ^{37}Cl	2863·0	2852·5	

transitions of the gas-phase spectrum. A weak induced '*Q*' feature is also seen, which may be compared with the spectra of gaseous HCl pressurised with Ar or N_2 gas[39] (Figure 3). A translational mode of HCl in noble gas matrices has been observed[40] in the far i.r. (at 73 cm^{-1} in argon), which is correlated with a weak band in the fundamental vibrational region assigned as $v + v_{\text{trans}}$ on the RTC model (see below), and recent work in these laboratories has found the

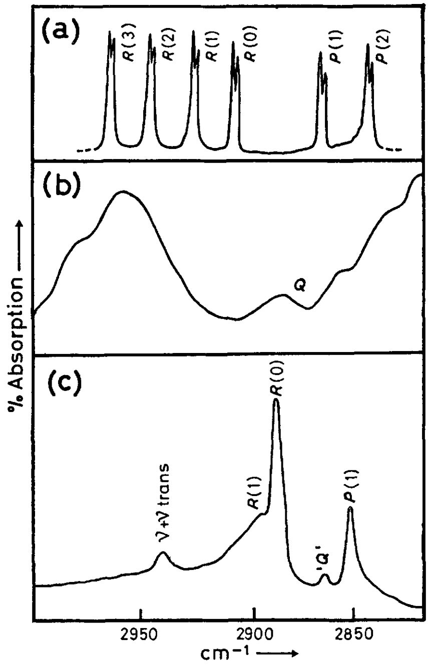

Figure 3 *I.r. spectra of hydrogen chloride* (a) *gas* (250 torr; 10 cm); (b) *gas* (1 atm.) *pressurised with* Ar (300 atm.), *redrawn from ref.* 39; (c) Ar *matrix* (M/A = 1000; 20°K)

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[39] H. Vu and B. Vodar, *Compt. rend.*, 1959, **248**, 2082.

[40] B. Katz, A. Ron and O. Schnepp, *J. Chem. Phys.*, 1967, **46**, 1926.

$J = 1 \leftarrow J = 0$ rotational absorption at 18 cm^{-1} for HCl in argon. Both these bands have additionally been observed for HCl trapped in a quinol cage at low temperature in the form of a HCl–quinol clathrate.[41] Confirmatory evidence of translational or rotational motion in noble gas matrices has also been found for HBr, HF, and H_2O in the far-i.r.[40,42,43] Certain small radicals appear to rotate in noble gas matrices, *e.g.* NH_2.[44] Discrete rotational structure has also been observed for the fundamental vibration band of HCl in a sulphur hexafluoride matrix,[45] but matrices other than the noble gases have not been used to any great extent, with the exception of nitrogen in which rotation does not seem to occur. From recent work on the hydrogen halides,[11] it would appear, in general, that rotation of small molecules occurs in any matrix which has a spherical cavity, but not in matrices, such as nitrogen, which have 'cylindrical' cavities. Two other effects which cause multiplet structure of bands in matrices are associated with rotation, and have been observed for H_2O, NH_3, and CH_4, namely inversion and nuclear spin conversion.

In principle the perturbation of the rotational levels of the solute molecule from the gas phase to the matrix environment should be capable of providing information about the intermolecular forces. Numerous attempts have been made to calculate the perturbation of the rotational levels of a diatomic molecule, in an inert matrix, in terms of a potential barrier to rotation,[46–49] or on a rotational–translational coupling (RTC) model;[22,50–53] the latter model assumes that the solute molecule is undergoing constrained translational motion in the matrix lattice, and treats this as a perturbation of the rotational motion. The hindered rotor model is successful in predicting the general trend of rotational spacings in noble gas matrices, and the splitting of the $J = 2$ level; it fails to predict the direction of the change in rotational spacing from HX to DX. The RTC model accounts satisfactorily for all observed spectral effects. Some theoretical work has also been done on tetrahedral molecules[54] as rotating solutes in inert matrices.

C. Vibrational Analysis.—Whilst the value of the matrix isolation technique when applied to stable molecules is not so obvious as its applications to reactive species, it still affords a number of advantages. In principle, at least, the spectrum

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[41] (*a*) S. J. Allen jun., *J. Chem. Phys.*, 1966, **44**, 394, 4654; (*b*) M. M. Davies, personal communication.

[42] D. W. Robinson and W. G. von Holle, *J. Chem. Phys.*, 1966, **44**, 410.

[43] D. W. Robinson, *J. Chem. Phys.*, 1963, **39**, 3430.

[44] D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, 1965, **43**, 4487.

[45] R. Ranganath, T. E. Whyte jun., T. Theophanides, and G. C. Turrell, *Spectrochim. Acta*, 1967, **23**, *A*, 807.

[46] A. F. Devonshire, *Proc. Roy. Soc.*, 1936, *A*, **153**, 601.

[47] R. L. Armstrong, *J. Chem. Phys.*, 1962, **36**, 2429.

[48] W. H. Flygare, *J. Chem. Phys.*, 1963, **39**, 2263.

[49] R. L. Armstrong, *J. Chem. Phys.*, 1966, **44**, 530.

[50] H. Friedmann and S. Kimel, *J. Chem. Phys.*, 1964, **41**, 2552.

[51] H. Friedmann and S. Kimel, *J. Chem. Phys.*, 1965, **43**, 3925.

[52] H. Friedmann and S. Kimel, *J. Chem. Phys.*, 1966, **44**, 4359.

[53] H. Friedmann and S. Kimel, *J. Chem. Phys.*, 1967, **47**, 3589.

[54] H. F. King and D. F. Hornig, *J. Chem. Phys.*, 1966, **44**, 4520.

of a substance in an inert matrix at very low temperatures should be simpler than its spectrum in any other phase since there is, in general, no rotational structure, crystal splitting, lattice modes, *etc.* Also, the small bandwidths at the low temperatures employed give a better chance of resolving bands close in frequency and the symmetry of the environmental interaction may allow degenerate levels to be resolved. Matrix isolation is thus useful in obtaining vibrational assignments, for example the 575 cm^{-1} gas-phase band of carbonyl chloride was found[55] to split into three bands (due to v_1, v_6, and $2v_3$) in an argon matrix. Our results on isotopic methanols in argon matrices[21] throw fresh light on the positions of the CH_3 rocking modes, and also the CH_3 asymmetric A' and A'' stretching and deformation frequencies could be distinguished: thus the CH_3 asymmetric stretching mode, at 2977 cm^{-1} in the gas phase, splits into two bands at 3005·3 (A') and 2961·9 cm^{-1} (A'') and similarly the bending mode, at 1477 cm^{-1} in the gas, splits into two bands at 1474·1 and 1465·8 cm^{-1}. Similarly, Durig, Bush, and Baglin found matrix-isolation experiments useful in an analysis of methylamine.[56]

D. Free Radicals and Unstable Molecules.—The matrix isolation technique was devised specifically for application to the study of free radicals, and has been widely used in this connection. The advantages are the comparatively easy stabilisation of highly reactive species for long periods, and the freedom from rotational structure (except for one or two small radicals such as[44] NH_2) which complicates gas-phase spectra (the only other convenient medium in which radicals may be obtained). The reactive species have normally been produced either by photolysis, *in situ*, of a single molecule or by the photolysis products of one molecule reacting with a second molecule. Thus, for example, the first such species to be characterised was HNO, produced by the photolysis of nitromethane in argon;[57] HCO has been produced by the photolysis of a mixture of HI and CO in argon,[58] HO_2 by the photolysis of HI or HBr and O_2 in argon,[58,59] *etc.* An alternative method of preparation involves the use of a reactive matrix (invariably CO), for example HCO from the photolysis of HI, HBr, or H_2S in a CO matrix.[60,61] In some cases, radicals have been produced by chemical reaction in the matrix, for example the methyl radical from CH_3X + Li in argon.[62,63] Typical examples from the extensive range of radicals and unstable molecules which have been produced and studied in this manner, listed in greater detail in ref. 9, are given in Table 3. It should be stressed, however, that because of the large number of species involved in the more compli-

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[55] E. Catalano and K. S. Pitzer, *J. Amer. Chem. Soc.*, 1958, **80**, 1054.
[56] J. R. Durig, S. F. Bush, and F. G. Baglin, *J. Chem. Phys.*, 1968, **49**, 2106.
[57] H. W. Brown and G. C. Pimentel, *J. Chem. Phys.*, 1958, **29**, 883.
[58] J. F. Ogilvie, *Spectrochim. Acta*, 1967, **23**, *A*, 737.
[59] D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, 1963, **38**, 2627.
[60] G. E. Ewing, W. E. Thompson, and G. C. Pimentel, *J. Chem. Phys.*, 1960, **32**, 927.
[61] D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, 1964, **41**, 3032.
[62] W. L. S. Andrews and G. C. Pimentel, *J. Chem. Phys.*, 1966, **44**, 2527.
[63] W. L. S. Andrews and G. C. Pimentel, *J. Chem. Phys.*, 1967, **47**, 3637.

Table 3 *Typical examples of free radicals studied in matrices*

Radical	*Produced by*	*Fundamental wavenumbers* (cm^{-1})	*Structure*
OH	Photolysis of H_2O in Ar or Kr	(Ar) $v = 3452$	
NH_2	Photolysis of NH_3 in Ar, N_2, or CO	(N_2) $v_2 = 1499$ $v_3 = 3220$ (v_1 unobserved)	bent
HNC	Photolysis of CH_3N_3 in Ar	(Ar) $v_1 = 2032$ $v_2 = 535$ $v_3 = 3583$	linear
HCO	Photolysis of HI + CO in Ar or photolysis of HI, HBr, or H_2S in CO	(Ar) $v_1 = 2482$ $v_2 = 1091$ $v_3 = 1862$	bent
CCO	Photolysis of N_3CN + CO in Ar or photolysis of C_3O_2 in Ar	(Ar) $v_1 = 1074$ $v_2 = 381$ $v_3 = 1978$	linear
Cl_3	Photolysis of Cl_2 in Kr	(Kr) $v_3 = 375$ (v_2 unobserved)	linear
CH_3	Photolysis of CH_4 in Ar or N_2 or reaction of CH_3X + Li, Na, or K in Ar	(Ar) $v_2 = 619$ $v_4 = 1383$ (v_3 unobserved)	planar
$SiCl_3$	Photolysis of $HSiCl_3$ in Ar, N_2, or CO	(Ar) $v_1 = 470$ $v_3 = 582$ (v_2 and v_4 unobserved)	pyramidal

cated systems, and the possibilities of multiple trapping sites, aggregation, *etc.*, considerable care should be exercised in interpreting the data.

E. Noble Gas Compounds.—Photolysis in a solid matrix also provides an ideal technique for the synthesis and i.r. investigation of noble gas compounds. The method is particularly suitable for the noble gas fluorides in view of the ease of dissociation of fluorine. Turner and Pimentel,[64,65] by photolysis of a mixture of krypton and fluorine diluted in an argon matrix, prepared KrF_2 and assigned bands at 580 cm^{-1} and 236 cm^{-1} to v_3 and v_2 respectively. Xe F_2 and Xe F_4 were prepared in a similar manner by using Xe in place of Kr. No evidence, however, could be found for the formation of any argon fluorides when fluorine alone in an argon matrix was irradiated.

Spratley[66] has also utilised the matrix isolation technique for the preparation of noble gas compounds and has confirmed the work of Turner and Pimentel. He further found no evidence of reaction between Xe and Cl_2, O_2 or O_3. However, $XeCl_2$ has since been produced in a matrix.[67] Hanlan[68] and Bassler, Timms,

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[64] J. J. Turner and G. C. Pimentel, *Science*, 1963, **140,** 974.

[65] J. J. Turner and G. C. Pimentel in 'Noble Gas Compounds', ed. H. H. Hyman, Chicago Univ. Press, Chicago, 1963.

[66] R. D. Spratley, Ph.D. Thesis, University of California, 1964.

[67] L. Y. Nelson and G. C. Pimentel, *Inorg. Chem.*, 1967, **6,** 1758.

and Margrave[69] could find no indications of the existence of BF_3–noble gas adducts in argon, krypton, and xenon matrices at 20°K.

F. High-temperature Species.—There is currently much interest in the chemical structures and properties of the vapour species in equilibrium with materials such as metal oxides and halides at high temperatures (several thousand degrees). Mass spectrometry has been widely employed to determine equilibrium data for gas–solid systems but unfortunately this approach does not provide any information concerning the structure of the gaseous species. Conventionally such information would be obtained by optical spectroscopy but there are, however, considerable experimental difficulties in observing the spectra of high temperature species in the gas phase. These are due mainly to the chemical reactivity of the vapour species with the containing cell and optical windows and the difficulty in obtaining a sufficiently high concentration of the vapour species in the optical beam. Furthermore, high temperature spectra are complicated by transitions involving populated high rotational and vibrational levels ('hot' bands). These difficulties are largely overcome by the matrix isolation technique which was first adapted to high temperature systems by Linevsky.[70] A molecular beam of the gaseous species, produced by the vaporisation of a refractory solid, is allowed to effuse from a Knudsen cell (Figure 4) into a vacuum and is then

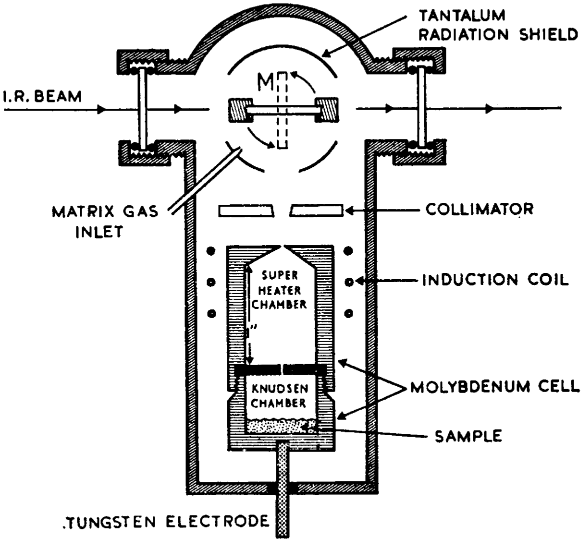

Figure 4 *Knudsen furnace and matrix isolation cell for examining high temperature species. The sample is inductively heated in vacuum and the vaporizing molecules are trapped in solid argon or krypton on the cold support window* M. (Reproduced from ref. 9 by permission of the Institute of Petroleum)

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[68] J. F. Hanlan, Ph.D. Thesis, University of California, 1961.
[69] J. M. Bassler, P. L. Timms, and J. L. Margrave, *J. Chem. Phys.*, 1966, **45**, 2704.
[70] M. J. Linevsky, *J. Chem. Phys.*, 1961, **34**, 587.

simultaneously condensed with a stream of inert matrix gas (usually argon or krypton) on to a cold window. The systems examined include the lithium halides, Group II metal halides, and a wide range of transition-metal oxides, listed in Table 4.

Table 4 *Vaporising molecules studied by matrix isolation*

Series	*Molecules studied*
Non-metallic compounds	C_{3-12}, Si_2C, Si_2C_3, SiC_2, B_2O_2, B_2O_3, BO_2
Alkali halides	LiF, LiCl, LiBr, LiI, NaF (and Li_2X_2 dimers, *etc.*)
Alkaline earth halides	BeF_2, $BeCl_2$, $BeBr_2$, BeI_2, MgF, MgF_2, CaF_2, SrF_2, BaF_2
Group IIB halides	ZnF_2, $ZnCl_2$, $ZnBr_2$, ZnI_2, $CdCl_2$, $HgCl_2$
First transition-series halides	ScF_3, ScF_2, $MnCl_2$, $FeCl_3$, $FeCl_2$, $CoCl_2$, NiF_2, $NiCl_2$, $NiBr_2$
Miscellaneous halides	AlF_3, AlF, $NbCl_5$
Alkali metal oxides	Li_2O, LiO, Li_2O_2, LiO_2
First transition-series oxides	ScO, TiO, TiO_2, VO, CrO
Second transition-series oxides	YO, ZrO, ZrO_2, NbO, MoO, MoO_x
Third transition-series oxides	LaO, HfO, TaO, TaO_2, WO, WO_x
Miscellaneous oxides	Al_2O, ThO, ThO_2, UO, UO_2

G. Analysis of Gas Mixtures.—A novel method for qualitative and quantitative analysis of multicomponent gas mixtures known as pseudo matrix isolation has recently been developed by Rochkind.[71,72] The method involves condensing the gas mixtures, diluted 100 : 1 with N_2, at 20°K by controlled-pulse deposition. This results in the isolation of individual species and the spectra are characterised by extremely sharp absorptions (Figure 5*b*). Such spectra contrast markedly with gas phase spectra with their rotational features (Figure 5*a*). Nitrogen is utilised as a matrix since to date no trapped molecule in this medium has been found to exhibit vibrational–rotational features.

A number of gases and volatile liquids in multicomponent mixtures has been investigated. These have been successfully analysed quantitatively since the sharp features presented at cryogenic temperatures rarely give rise to problems of band overlap. The technique appears to be far superior to gas chromatography for the quantitative analysis of isotopic isomers (in μmole quantities), such as deuteriated ethylenes, and thus has promising applications in cryogenic photochemistry.

The method must be treated with caution, however, since it pre-supposes either that effects such as incomplete condensation and intermolecular interactions will affect all species equally, or that such effects are negligible.

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[71] M. M. Rochkind, *Analyt. Chem.*, 1967, **39**, 567.
[72] M. M. Rochkind, *Analyt. Chem.*, 1968, **40**, 762.

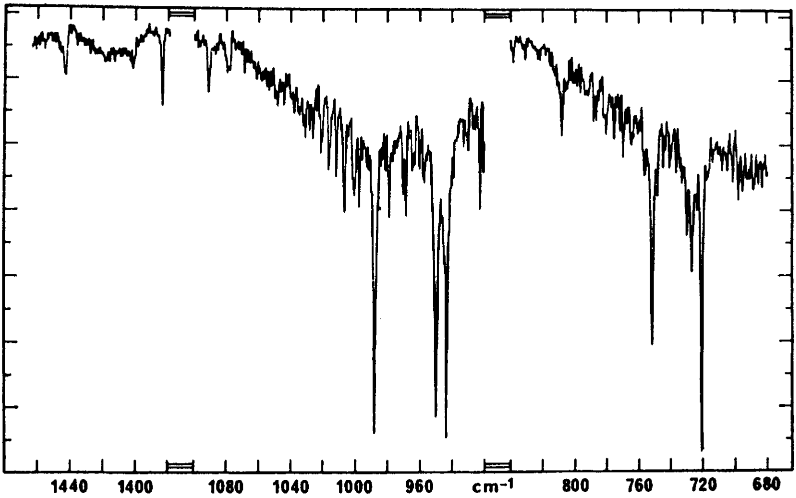

Figure 5a *Gas phase spectrum of mixture of deuteriated ethylenes:* ~30 torr, 10-cm *path. Mixture composition* ca.: 5 *parts ethylene,* 1 *part* [^{2}H]*ethylene,* 3 *parts* [1,1-$^2H_2$]*ethylene,* 3·5 *parts* [trans 1,2-$^2H_2$]*ethylene,* 2·5 *parts* [$^2H_4$]*ethylene. Spectral slit:* ~0·7 cm^{-1}. (Reproduced from ref. 72 by permission of *Analyt. Chem.*, 1968, **40**, 762)

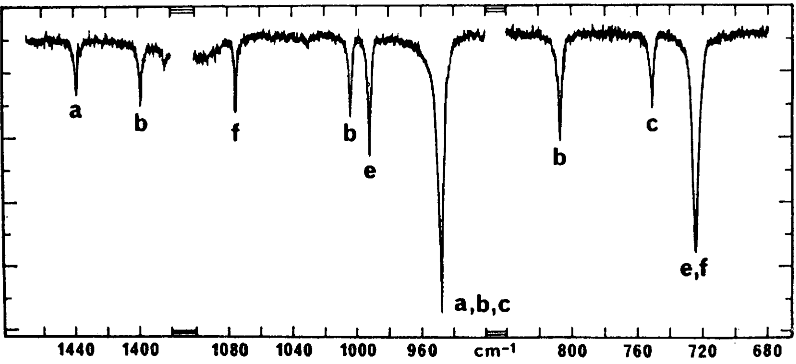

Figure 5b *Infrared pseudo matrix isolation spectrum,* 20°K, *of mixture of deuteriated ethylenes* (1%) *in nitrogen. Mixture composition was:* 0·7 *parts ethylene* (a), 1 *part* [^{2}H]*ethylene* (b), 0·5 *parts* [1,1-$^2H_2$]*ethylene* (c), 0·7 *part* [trans 1,2-$^2H_2$]*ethylene* (e), 1·4 *parts* [$^2H_4$]*ethylene* (f). *A total of* 14·7 μmoles *of ethylenes was deposited in three* ca. 0·5 mmole *pulses. Spectral slit:* ca. 0·9 cm^{-1} (Reproduced from ref. 72 by permission of *Analyt, Chem.*, 1968, **40**, 762)

4 Theories of Matrix Shifts

The frequency of the band (centre) in condensed phases is generally displaced below the gas-phase value, owing to specific and non-specific interactions with the surrounding molecules. The effect of the environment on i.r. absorption frequencies of substances in (liquid) solution has been extensively studied,[73]

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[73] H. E. Hallam in 'Spectroscopy', ed. M. J. Wells, Inst. of Petroleum, London, 1962, p. 245.

and is interpreted in terms of specific solute–solvent dipolar interactions, particularly $\mathrm{R} - \overset{\delta+}{\mathrm{H}} \cdots \overset{\delta-}{\mathrm{S}}$, superimposed on non-specific (inductive and dispersive) contributions. Various theories have been put forward to account for the solvent shifts, based on a model of the solute as a point dipole in a spherical cavity within the solvent medium of uniform dielectric constant ϵ' and refractive index n, for example:

Kirkwood-Bauer-Magat[74,75]

$$\frac{\Delta v}{v} = C\,\frac{(\epsilon' - 1)}{(2\epsilon' + 1)} \tag{1}$$

Buckingham[76]

$$\frac{\Delta v}{v} = C_1 + \tfrac{1}{2}(C_2 + C_3)\,\frac{(\epsilon' - 1)}{(2\epsilon' + 1)} \text{ (non-polar solvents)} \tag{2}$$

$$\frac{\Delta v}{v} = C_1 + C_2\,\frac{(\epsilon' - 1)}{(2\epsilon' + 1)} + C_3\,\frac{(n^2 - 1)}{(2n^2 + 1)} \text{ (polar solvents)} \tag{3}$$

David and Hallam[77]

$$\frac{\Delta v}{v} = C'_1 + C'_2\,\frac{(\epsilon' - 1)}{(\epsilon' + 2)} + C'_3\,\frac{(n^2 - 1)}{(n^2 + 2)} \tag{4}$$

Caldow and Thompson[78] attempted to take account of specific interactions by adding a fourth term to eqn. (3), namely $C_4\sigma^*$, where σ^* is the Taft inductive factor for the residue R of a solvent RH.

The theories developed to deal with the vibrational shifts in solution should be capable of being extended to cover matrices, the only difference being that in the case of matrices the solute molecule is held in a rigid 'cage', giving rise to the possibility that repulsive forces may play an important role.

Several attempts have been made to analyse the matrix-induced frequency shifts of diatomic molecules by direct summation of the interactions between the point polar solute molecule and the polarisable molecular cage. The intermolecular potential energy may be expressed as the sum of four terms, arising from electrostatic, inductive, dispersive, and repulsive contributions, and thus the shift is given by

$$\Delta v = (v_m - v_g) = \Delta v_{\text{elec}} + \Delta v_{\text{ind}} + \Delta v_{\text{dis}} + \Delta v_{\text{rep}} \tag{5}$$

The electrostatic contribution is, of course, zero for non-polar matrices such as argon, since it arises from the interaction between the permanent charge distributions of the solute and matrix molecules. Even where the matrix molecule has a quadrupole, *e.g.* nitrogen, the electrostatic shift cancels to zero because of the symmetry of the f.c.c. lattice, assuming that the solute molecule occupies a substitutional site.

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[74] W. West and R. T. Edwards, *J. Chem. Phys.*, 1937, **5**, 14.

[75] E. Bauer and M. Magat, *J. Phys. Radium*, 1938, **9**, 319; *Physica*, 1938, **5**, 718.

[76] A. D. Buckingham, *Proc. Roy. Soc.*, 1958, *A*, **248**, 169; 1960, *A*, **255**, 32; *Trans. Faraday Soc.*, 1960, **56**, 753.

[77] J. G. David and H. E. Hallam, *Spectrochim. Acta*, 1967, **23**, *A*, 593.

[78] G. L. Caldow and H. W. Thompson, *Proc. Roy. Soc.*, 1960, *A*, **254**, 1.

The inductive effect arises from the interaction between the permanent charge distribution of one molecule, and the moments induced in the other molecule. On the basis of a point polarisable atom model,[79] the shift is given by:

$$\Delta\nu_{\text{ind}} = -\frac{N_6\,\alpha_b}{hc\,d_0^6}\,\Delta(\mu_a^2) \tag{6}$$

assuming that the solute molecule occupies a substitutional site, diameter d_0, in the matrix lattice; N_6 is the effective number of nearest neighbours for an r^{-6} law (14·454 for a f.c.c. lattice[80]); μ_a is the dipole moment of the solute molecule and α_b the polarisability of the matrix molecule.

On the basis of a cavity model,[81] the shift is given by

$$\Delta\nu_{\text{ind}} = -\frac{8(\epsilon'-1)}{(2\epsilon'+1)hcd_0^3}\,\Delta(\mu_a^2) \tag{7}$$

In both cases, terms involving solute moments higher than the dipole are neglected. Both models are unrealistic, the p.p.a. model underestimating, and the cavity model overestimating, short-range interactions with nearest neighbours actually in contact with the solute molecule.

Using a Lennard-Jones–Devonshire cell model, Friedmann and Kimel[51] give expressions for the dispersive shift (due to attraction between the instantaneous charge distributions of the solute and matrix molecules):

$$\Delta\nu_{\text{dis}} = -\frac{4}{hc}\,N_6\,\epsilon(x)_0\left[\frac{\sigma(x)_0}{d_0}\right]^6 F(\alpha) \tag{8}$$

and for the repulsive shift (due to overlap of the electronic charge distributions):

$$\Delta\nu_{\text{rep}} = \frac{4}{hc}\,N_{12}\,\epsilon(x)_0\left[\frac{\sigma(x)_0}{d_0}\right]^{12}[F(\mu)+F(\alpha)]\left(\frac{2+y}{1+y}\right) \tag{9}$$

where $F(\alpha) = \dfrac{\alpha_a(x)_v - \alpha_a(x)_0}{\alpha_a(x)_0}$,

$$F(\mu) = \frac{\mu_a(x)_0\,\alpha_b}{2\epsilon(x)_0\sigma^6(x)_0}\,[\mu_a(x)_v - \mu_a(x)_0]\,,$$

$\epsilon(x)_v$ and $\sigma(x)_v$ are v-dependent (v is the vibrational state of the solute molecule) Lennard-Jones parameters, y is a molecular parameter, and $N_{12} = 12{\cdot}132$ for a f.c.c. lattice.

Friedmann and Kimel[51] also give expressions for a dynamic shift, caused by the translational motion of the solute molecule (see above), but this is negligible (*ca.* 1 cm^{-1}).

Because of the limited number of (solvent) matrices employed it is too soon to say how successful these relationships are in predicting total shifts. A recent study[11] of a wider range of matrices—such as CH_4, SF_6, CO, C_2H_4—indicates,

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[79] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, 'Molecular Theory of Gases and Liquids', Wiley, New York, 1954.

[80] J. E. Lennard-Jones and A. E. Ingham, *Proc. Roy. Soc.*, 1925, *A*, **107**, 636.

[81] D. C. McKean, *Spectrochim. Acta*, 1967, **23**, *A*, 2405.

however, that this approach gives results of the correct order of magnitude for matrices with spherical cavities, but that some account will need to be taken of the shape of the cavity if it is to be successfully applied to matrices with 'cylindrical' cavities.

5 Future Prospects

Although the matrix isolation technique was originally devised for application to unstable species, and the majority of the work to date has been done in this field, there is an increasing interest in stable molecules. It would appear to be the ideal state to study the vibrational spectra of molecules for force constant analysis, thermodynamic properties, *etc.* Such studies would need to be augmented by Raman spectra—to date only one Raman study[36] of a matrix-isolated species, CH_4, has been reported.

The potential energy barriers to rotation about single bonds are usually less than *ca.* 5 kcal and the resulting torsional vibrations lie in the far-i.r. region. The centres of these absorption frequencies are sometimes difficult to locate owing to the superposition of hot bands. As has been pointed out by Wood[82] these could be greatly improved by trapping the molecules in an inert matrix at low temperature. Barrier heights calculated from torsional-vibration frequencies could thus be determined with greater precision.

The use of a wider range of matrices, especially more polar ones, will increase our knowledge of solute–matrix interactions, while the study of the interactions (or even reactions) between different solute molecules in inert matrices opens up a wide field of study. With the increasing availability of cryogenic facilities it is certain that the matrix-isolation method will become a routine technique in spectroscopic laboratories.

We thank the Hydrocarbon Research Group of the Institute of Petroleum for a research studentship (to A.J.B.).

[82] J. L. Wood, *Quart. Rev.*, 1963, **17**, 362.