INFRARED SPECTRAL PERTURBATIONS IN MATRIX EXPERIMENTS

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INTRODUCTION

The matrix isolation technique is now well established as a spectroscopic technique. The number of practitioners using the infrared spectral region is growing and there have been a number of rather sure identifications of unusual species. *Table 1* lists those now reported, the mode of preparation, and the authors.

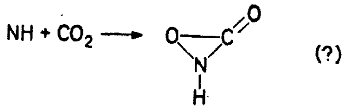
Table 1. Unusual molecular species identified through infrared matrix studies

Molecule	*Mode of preparation*	*Reference*
HNO	$CH_3NO_2 + h\nu \rightarrow HNO + CH_2O$	1
	$H + NO \rightarrow HNO$	2
	$NH + CO_2 \rightarrow HNO + CO$	3
iso-N_2O_4	$2\ NO_2(g) \rightarrow i\text{-}N_2O_4$	4, 5
HCO	$H + CO \rightarrow HCO$	6
LiF	$LiF(g) \rightarrow LiF$	7
NCl	$ClN_3 + h\nu \rightarrow ClN + N_2$	8
NF_2	$N_2F_4 + \text{heat} \rightarrow 2\ NF_2$	9

In addition, there have been a substantial number of studies in which unusual reactions have been discovered. These demonstrate unique possibilities in the study of the reactions and production of extremely reactive species. A number of these have been listed in the literature[10] and only two recent examples will be mentioned. Milligan and Jacox[11] photolysed methyl azide in solid nitrogen to produce $CH_2{=}NH$.

$$CH_3N_3 + h\nu \rightarrow CH_2{=}NH + N_2$$

In another study, Milligan *et al.*[3] reacted NH with solid CO_2 matrix, possibly to form an unusual cyclic compound.



All of these interesting studies are made more difficult by the lack of a complete understanding of the influence of the matrix environment on a vibrational spectrum. This can be helped only through the more prosaic, but equally fundamental, spectral studies of stable molecules under matrix conditions. These turn out to be of substantial interest in their own right, by raising and, it is hoped, ultimately answering, interesting questions concerning intermolecular forces in the solid state.

There are a variety of aspects of the spectra that need consideration. Absorption frequencies and absorption coefficients differ somewhat from gas-phase values. The effects are relatively small, as could be expected from the wide experience with solution spectra. Less usual are effects that cause multiplet absorptions, presumably visible in matrix spectra because of such factors as lattice regularity and extremely low temperature. Such multiplet splittings have been observed by a number of workers and they have been variously interpreted. All of these matrix disturbances interfere with identification of unusual molecular species and they all contain information about intermolecular forces.

We will consider here frequency shifts and multiplet splittings. To put bounds on the subject area, the discussion will be confined to the commonly used matrix materials that are gases under normal conditions. Most information is available for nitrogen and argon.

FREQUENCY SHIFTS

Experimental data

Table 2 collects matrix frequencies for 18 vibrational frequencies of 13 molecules. The data were selected because the identification is certain, the gas phase frequencies are well known, the matrix frequencies are uncertain by less than ± 2 cm^{-1}, and there are no known " multiplet " complications. *Table 3* lists matrix shifts in solid nitrogen for the vibrations of *cis-trans*-nitrous acid. *Table 4* contrasts the frequency shifts of four of the vibrational modes of hydrazoic acid in six different matrices.

The data for solid nitrogen are most numerous and, hence, most informative. *Tables 2, 3,* and *4* contain 16 frequency shifts (in nitrogen) for stretching modes and 12 shifts for bending or torsional modes. Among these data, the average magnitude of $\Delta\nu$ is 9 cm^{-1} for a stretching mode and it is 13 cm^{-1} for a bending mode. More striking, however, is the absolute average, taking account of sign. The stretching modes average -3 cm^{-1}, whereas the bending modes average $+10$. Among the 16 stretching modes, only 6 show positive shifts and the range is from $+21$ to -32. Among the 12 bending modes, 7 show positive shifts and the range is from $+40$ to -6.

The data for solid argon are less numerous but seem to be similar to the results for nitrogen. *Table 5* contrasts the averages for the two matrix materials. The data suggest that bending modes tend to be shifted by nitrogen preferentially toward higher frequencies. In contrast, stretching vibrations tend to be shifted towards lower frequencies but positive shifts are not uncommon, either in nitrogen or in argon. Furthermore, the absolute magnitude of the shifts is larger for the bending modes.

This apparent difference between stretching and bending modes may not be significant. *Figure 1* shows a plot of frequency shift against the band frequency. Despite the large scatter, there is a general trend, as suggested by

Table 2. Experimental frequency shifts

		$\Delta\nu = \nu_{mx} - \nu_{gas}$						
			N_2		Ar		Other mx	
Molecule	*Vibration**	ν_{gas}†	ν_{mx}‡	$\Delta\nu$	ν_{mx}	$\Delta\nu$		$\Delta\nu$
NO	st	1876 (ref. 13)	1876	0	1875	−1	CO_2	+7 (ref. 4)
N_2O	s. st	1285·0	1292	+7	—			
	a. st	2223·5	2240	+7	2228 (ref. 15)	+5		
NO_2	a. st	1616 (ref. 16)	1616	0	1611 (ref. 4)	−5	CO_2	+8 (ref. 4)
CO_2	b	667·3	661	−6	—			
	a. st	2349·3	2340	−9				
H_2O	b	1595·0	1599	+4			CO_2	+20 (ref. 17)
NH_3	s. st	3336·2 (ref. 18)	3332 (ref. 19)	−4				
	a. st	3443·7 (ref. 18)	3440 (ref. 19)	−4				
	s. bend	950·0 (ref. 18)	970 (ref. 19)	+20				
C_2H_2	op. b	729·1			740 (ref. 15)	+11		
C_2D_2	a. st	2427			2418 (ref. 15)	−9		
CH_4	a. b	1306·2	1304 (ref. 20)	−2				
CH_3D	b	1156·0	1155 (ref. 20)	−1				
	b	1306·4	1304 (ref. 20)	−2				
CH_3I	b	1251·5	1248 (ref. 20)	−4				
CH_2CO	CO st	2151 (ref. 21)			2142 (ref. 15)	−9		
C_2H_4	op. b	949·2	960	+11				

* st = stretch, b = bend, s = symmetric, a = asymmetric, op = out-of-plane.
† Reference 12 unless otherwise indicated.
‡ Reference 14 unless otherwise indicated.

Table 3. Experimental frequency shifts, nitrous acid in N_2

	T = 20°K, $\Delta\nu = \nu_{mx} - \nu_{gas}$					
	cis-HONO			*trans*-HONO		
*Vibration**	ν_{gas}†	ν_{mx} (ref. 14)	$\Delta\nu$	ν_{gas}†	ν_{mx} (ref. 14)	$\Delta\nu$
ν_1 OH st	3426	3410	−16	3590	3558	−32
ν_2 N=O st	1639 (ref. 23)	1633	− 6	1696	1684	−12
ν_4 NO st	856	865	+ 9	794	815	+21
ν_5 ONO b				598	625	+27
ν_6 t	637	658	+21	543	583	+40

* st = stretch, b = bend, t = torsion.
† Reference 22 unless otherwise indicated.

Table 4. Experimental frequency shifts: HN_3 in various matrices[17]

$\Delta\nu = \nu_{mx} - \nu_{gas}$

Mode	N—H st	N—N—N a. st	N—N—N s. st	NNH b
ν_{gas}	ν_1 3335·6	ν_2 2140·4	ν_3 1269·0	ν_4 1152·5
Matrix	$\Delta\nu_1$	$\Delta\nu_2$	$\Delta\nu_3$	$\Delta\nu_4$
Ar	−12	− 2	− 5	− 6
Kr	−15	0	− 3	− 4
Xe	−37	− 8	− 6	− 7
N_2	−13	+ 8	+ 3	+15
CO	−41*	—	+15	+25
CO_2	−31*	+26*	+18	+35

* Matrix frequency uncertain to ±5 cm^{-1}.

Table 5. Average frequency shifts in nitrogen and argon matrices

	Stretching modes				*Bending modes*			
Matrix	*No. examples*	av $\lvert\Delta\nu\rvert$ (cm^{-1})	av $\Delta\nu$ (cm^{-1})	*Range* (cm^{-1})	*No. examples*	av $\lvert\Delta\nu\rvert$ (cm^{-1})	av $\Delta\nu$ (cm^{-1})	*Range* (cm^{-1})
N_2	16	9	−3	+21 to −32	12	13	+10	+40 to −6
Ar	8	6	−5	+5 to −12	2	9	+ 3	+11 to −6

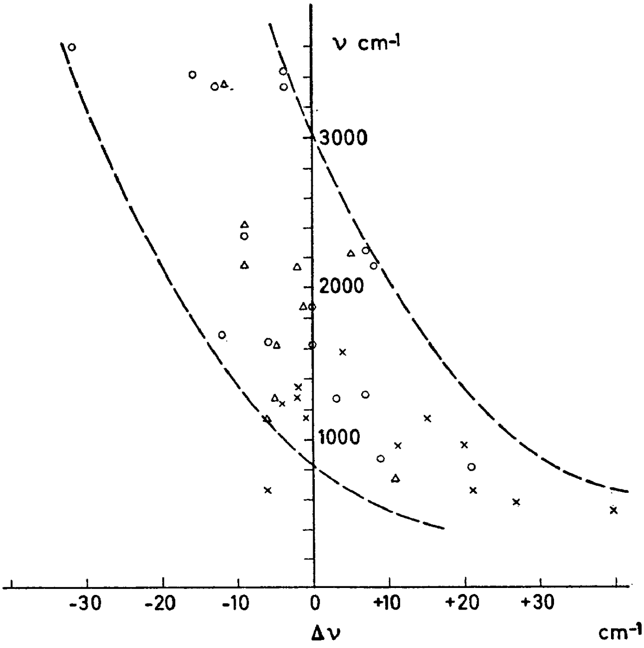


Figure 1. Matrix-induced frequency shifts in polyatomic molecules: $\Delta\nu$ *v.* ν

$\Delta\nu = \nu_{mx} - \nu_{gas}$

○ — stretching modes, N_2 matrix

× — bending, torsional modes, N_2 matrix

△ — stretching and bending modes, Ar matrix the dashed lines, for the shift to be more positive as frequency drops. On this plot, the distribution of the circles (data for stretching modes) seems to overlap reasonably the distribution of the crosses (data for bending modes). The triangles show the argon data and they, too, fall among the other points.

The contrast of HN_3 shifts in various matrices is challenging. First, the shifts observed in krypton do not fall between the corresponding values in argon and xenon. Second, the three modes ν_2, ν_3, and ν_4 behave quite differently in the inert gases than in the molecular matrices N_2, CO, and CO_2. Two of the obvious similarities of the last three that distinguish them from the inert gases is that they are not monatomic and they all have sizeable quadrupole moments.

Some unusual shifts

There are some examples of unusually large shifts that attract attention. Some of these were not included in the tables because they do not conform to one or more of the criteria specified, particularly certainty of identification and isolation.

HONO *in* N_2—There are two unanticipated aspects of the data shown in *Table 3.* All of the shifts of the *trans-* form are larger than those of the *cis-*form. In addition, the shift of the ν_6 torsional mode is distinctively large. Presumably the general trend toward larger shifts for the *trans* molecule indicates the effect of the shape of the molecule. It is conceivable that the nitrogen lattice is able to accommodate the compact *cis*-form more readily than the *trans*-form.

LiF *in* Ar, Kr, Xe, *and* N_2—Linevsky[7] has reported the vibrational spectrum of lithium fluoride under matrix conditions. He observes large frequency shifts: in Ar, -60 cm^{-1}; in Kr, -70 cm^{-1}; in Xe, -77 cm^{-1}; in N_2, -122 cm^{-1}. These shifts are all based on the gas phase frequency reported to be about 900 cm^{-1} by Vidale[24]. Assuming that the spectral features do correspond to isolated (monomeric) LiF molecules and that the gas-phase frequency is correct, these shifts are not at all compatible with the ones shown in the earlier tables. An obvious possibility is that the highly ionic character of the LiF molecule interacts primarily through a large dipole-induced dipole interaction (as suggested by Linevsky) and that this term is much less important in the examples of relatively covalent molecules listed earlier. Whatever the explanation, the LiF data suggest that ionic molecules may show extreme deviations from trends discovered among covalent molecules.

ClNO *in* Cl_2 *and in* Br_2—Hisatsune and Miller[25] have reported spectra of ClNO in Cl_2 and in Br_2 which are noteworthy because of extremely large frequency shifts from the gas phase. *Table 6* shows their assigned frequencies

Table 6. Frequencies of ClNO in Cl_2 and in Br_2[25]

		$T = 80 - 90°$			
Vibration	ν_{gas} (cm^{-1})	$\nu_{mx}(Cl_2)$ (cm^{-1})	$\Delta\nu(Cl_2)$ (cm^{1-})	$\nu_{mx}(Br_2)$ (cm^{-1})	$\Delta\nu(Br_2)$ (cm^{-1})
ν_1 N=O st	1800	1944	+144	1954	+154
ν_2 N—Cl st	596	493	−103	462	−134

and the implied shifts. As Hisatsune and Miller point out, ClNO has a vibrational spectrum that is particularly sensitive to environment. They conclude that their observations are best interpreted in terms of a definite chemical interaction—a weak complex—between, for example, Cl_2 and ClNO.

Theoretical aspects

Buckingham[26] has presented a perturbation treatment of the effect of a solvent environment on the vibrational frequencies of a diatomic molecule. He obtains

$$\nu_{\text{solvent}} - \nu_{\text{gas}} = \frac{B_e}{hc\omega_e}\left[U'' - 3\,\frac{A}{\omega_e}\,U'\right] \tag{1}$$

$B_e = h/8\pi^2 m_r c r_e^2$
$c\omega_e$ = Harmonic oscillator frequency for normal vibration Q
U = Energy due to solute–solvent interaction
$U = U_e + U'Q + \frac{1}{2}U''Q^2 + \ldots$
A = Anharmonicity constant

Expression (1) is more conveniently written in the form:

$$\Delta\nu = \frac{1}{4\pi c r_e^2\sqrt{m_r k}}\left[U'' - \frac{3A}{\omega_e}\,U'\right] \tag{2}$$

m_r = reduced mass

We are concerned here with polyatomic molecules, for which the expansion of U is more complicated.

$$U = U_e + \sum_k U_k'Q_k + \tfrac{1}{2}\,\Sigma\, U_{kl}''Q_kQ_l + \ldots \tag{3}$$

Here U''_{kl} is the derivative $\partial^2 U/\partial Q_k \partial Q_l$ where Q_k and Q_l are the k^{th} and l^{th} normal vibrations. Now expression (2) will include, for a given absorption ν_i, derivative contributions from the internal coordinates that make up ν_i. Qualitatively, however, we can expect the sort of dependence upon reduced mass, potential function, and sensitivity of the potential function to the vibration (through U'' and U') that is indicated in (2).

We shall proceed, then, to attempt to analyse the qualitative behaviour observed for the polyatomic molecules on the hopeful assumption that (2) exposes the factors of importance. In particular, we observe an apparent trend of increasing $\Delta\nu$ with decreasing ν. Frequencies are lowered by a rise in reduced mass and a reduction in force constant. We see in (2) that a rise in reduced mass produces the wrong effect on $\Delta\nu$. Lowering k, on the other hand, does raise $\Delta\nu$. In general, bending modes and torsional modes do have rather low force constants, so this may contribute to the apparent inverse dependence of $\Delta\nu$ and ν. The second derivative, U'', remains to be considered.

Figure 2 represents a bent triatomic molecule ABC positioned in a matrix cage. The nucleus of the matrix atom M that is the nearest neighbour to C is shown and indicated to be more-or-less rigidly positioned by the lattice. We shall consider the contribution to the energy U that results from the interaction of C and M, as it is influenced by the change in the internal coordinate r_{BC}. We shall ignore for the moment the movements and interactions of the other atoms, considering only the displacement of atom C.

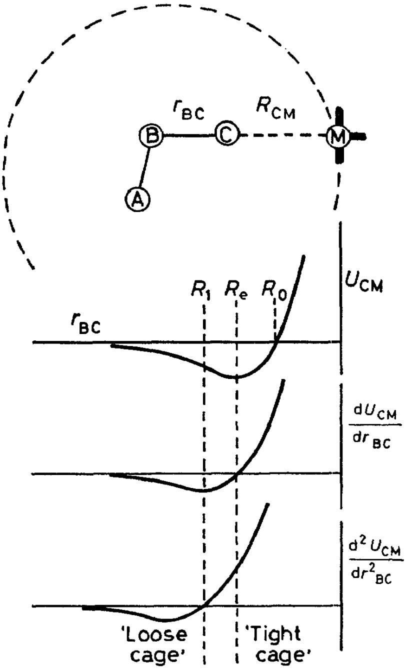


Figure 2. Dependence of U, U', and U'' upon matrix cage size

The functions U_{C-M}, $\partial U/\partial r_{BC}$, and $\partial^2 U/\partial r^2_{BC}$ are shown in *Figure 2c*. We see that if atom C is lodged a distance from M less than R_1, the effect of the matrix is to contribute a positive quantity to U'', tending to make $\Delta\nu$ greater than zero. If C is more distant from M than R_1, the sign of the effect is reversed, and the contribution to $\Delta\nu$ is negative.

On the other hand, the first derivative receives a positive contribution only if R_{CM} is less than R_e. We see, then, that for R_{CM} *less than* R_e (the optimum distance), both U'' and U' are positive. Since the anharmonicity constant A is a negative number, under these conditions both U'' and U' contributions give positive shifts. We shall refer to this type of positioning, $R_{CM} < R_e$, as a "tight cage".

For $R_{CM} > R_1$, the situation is reversed. At these large distances, both curvature and slope are negative, so they both contribute so as to give negative shifts. We shall refer to this type of positioning, $R_{CM} > R_1$, as a " loose cage ".

The observed trend of $\Delta\nu$, then, can be interpreted to mean that the high frequency vibrations tend to occur in a " loose cage " environment, whereas the low frequency vibrations tend to occur in a " tight cage ". A rationale for such an effect can be framed. Triatomic molecules and larger do not fit comfortably in a single substitutional site. In general, we can expect that the impurity must accept a lowest energy position that is a compromise between optimum distances at some points of contact with the matrix and less than optimum distances at other points. There will be a tendency for the matrix to distort the molecule to fit the available cage and the extent to which a given internal coordinate is distorted will depend upon the force constant associated with that coordinate. The low force constant coordinates will tend to be the ones that will find themselves in a " tight cage " as the matrix seeks out the lowest energy means of forcing the molecule to fit in the available matrix cage. These are the coordinates that participate in the low frequency vibrations, so there will be a general tendency for high frequency vibrations to show the negative shifts of a " loose cage " and low frequency vibrations to show the positive shifts of a " tight cage ".*

A natural question that comes to mind is, " Why hasn't this effect been noticed in liquid solutions under normal conditions? " A possible answer is that the liquid state at normal temperatures is, inherently, always a " loose cage ". The thermal agitation tends to keep the AB molecules somewhat farther separated from the solvent molecules than the optimum, and this emphasizes the region of interaction in which U'' and U' have opposite sign or are both negative. This would tend to give a larger percentage of shifts toward lower frequencies.

SPECTRAL COMPLICATIONS: INTERPRETATIONS OF MULTIPLETS

The several examples cited in *Table 3* show that numerous workers have found themselves confronted with multiplet features. There are three popular explanations—aggregation, rotation (free or hindered), and multiple sites. These will be taken up in turn.

Aggregation

When a molecule R is suspended in a matrix M, the spectrum of R is affected by the matrix cage. If the cage is exclusively M, a spectrum characteristic of the interaction of R with M is obtained. If the cage includes one molecule of R, the spectrum may be altered noticeably because the two adjacent R molecules are identical oscillators. The effect may increase if the

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* Another avenue of explanation that comes to mind naturally is that of the amplitude of oscillation. The average square displacement of a harmonic oscillator increases as the force constant is lowered.

$$\bar{x}^2 = \frac{h}{4\pi\sqrt{(mk)}} \tag{4}$$

Using a R^{-12}–R^{-6} type of potential function and reasonable van der Waals distances, one can show that the changing amplitude of vibration is not likely to account for the large effects to be explained.

cage contains two R molecules. This type of effect we refer to as an effect of aggregation.

Obviously the various cages, pure M, all M but one R, all M but two R, *etc.* can be described as " multiple sites ". We shall, however, segregate this type of multiple site behaviour on the assumption that persons who have invoked the multiple site explanation have in mind something more interesting than their inability to isolate the molecule of interest in the matrix.

There are some well-substantiated cases of aggregation. They involve hydrogen bonding substances, purposely studied to reveal aggregation in the characteristic and large shifts that accompany hydrogen bond formation. The cases of CH_3OH in N_2[27] and H_2O in N_2[28] were used as tests of isolation efficiency in the Berkeley laboratories in our development of technique. They need not be discussed because the experiments have been available in the literature for five years.

NH_3 *in* N_2—The case of NH_3 in N_2 was in controversy for some time. Multiplet features in the ν_2 spectral region were attributed to inversion and rotation by Milligan, Hexter, and Dressler[29], disagreeing with the earlier interpretation of Van Thiel that these could be attributed to polymeric ammonia aggregates[30]. Bulanin repeated Van Thiel's study much more carefully and definitely showed that the multiplet features disappeared as the concentration was reduced, confirming the aggregation interpretation[31].

CO *in* Ar—Recent studies in the Berkeley laboratories of CO in argon seem to show that aggregation provides obvious spectral splittings[32, 33]. The principal absorptions of CO in Ar are found at 2148 and 2138 cm^{-1} with intensities varying from experiment to experiment. Careful control of deposition conditions is needed to obtain reproducibility. When conditions are controlled, the higher frequency becomes dominant as concentration is lowered, showing that the lower frequency is caused by aggregates. Temperature changes (from 20 to 4 to 20 °K) showed no effects that suggest rotation. Isotopic effects are consistent with the aggregation interpretation. Finally, the feature attributed to CO aggregates, 2138 cm^{-1}, is quite close to the absorption of CO in pure CO[33], 2138·4 cm^{-1}, as might be expected.

In conclusion, our experience leads us to state that it is surprisingly difficult to prevent aggregation and achieve complete isolation, even at matrix-to-impurity mole ratios above 500 and that failure to prevent aggregation *usually* results in observable spectral effects—most often broadening, sometimes slight shifts, sometimes multiplets. It would seem unwise ever to propose an interpretation of multiplets *until* the effect of varying concentration had been studied systematically to eliminate the relatively unexciting but quite likely possibility that aggregation (incomplete isolation) accounts for the multiplets observed.

Rotation, free or hindered

Rotational fine structure in matrix spectra would be extremely informative concerning intermolecular forces. At the Berkeley laboratories, we have searched for evidence of rotational freedom for several years now. Only two examples were encountered and these will be mentioned below. On the other hand, we have *never* found evidence for rotational freedom in a nitrogen matrix, though we have studied perhaps two dozen molecules in this matrix.

Robinson and McCarty are probably the first to claim evidence of free rotation in matrix studies. In their detection of argon-trapped NH_2, using electronic spectroscopy[34, 35], they observed some 67 features in the spectral region 12661 to 29012 cm^{-1}. In this region they list some 24 absorption features of gaseous NH_2 and are able to find one of their 67 lines within about 30 cm^{-1} of each of the 24. The correlation includes 8 of the 10 most intense bands observed by Robinson and McCarty (though only 9 of the 20 most intense). They conclude that " NH_2 radicals are undergoing nearly free end-over-end rotations in the solid phase ". The samples studied by Robinson and McCarty used mole ratios of matrix-to-parent molecule of 25 to 1. The parent molecules, NH_3 or N_2H_4, were passed through a glow discharge and then deposited at 4 °K.

Since this proposal was made, other workers, using infrared evidence, have postulated free or hindered rotation. We will restrict our attention to the studies based on infrared spectra.

H_2O *in* Ar, Kr, *and* Xe—Though the bending mode of H_2O in solid nitrogen absorbs in a single, sharp feature, Catalano and Milligan[36] discovered that H_2O in the inert gases gives multiplets in the region of ν_2. Variations of concentration did not remove the structure. For argon matrix, they list eight features between 1554 and 1685 with irregular spacings between 13 and 20 cm^{-1}. D_2O in argon also shows the multiplet splitting and the spacings are smaller: 5 to 15 cm^{-1}. Temperature changes between 4 and 20 °K altered relative intensities. Catalano and Milligan were not able to interpret in detail the spectra but conclude qualitatively that rotation is the likely explanation though " it may not be unrestricted rotation ".

Their analysis seems correct. The most likely interpretation does seem to be that water has considerable librational freedom in the inert gases. That free rotation is not involved is indicated by the absence of a gap due to an inactive Q branch.

The spectral region of the stretching modes was investigated later by Glasel[37]. He studied H_2O in argon and xenon and concludes that the several features observed are attributable to *ortho* and *para* modifications of H_2O rotating in these two matrices. There are some difficulties in the study—there is interference from dimeric absorption. Some of the relative intensities are awry—Glasel points out that two of the features in argon show a relative intensity of 6:1 whereas 1:4 is expected. All of the spectral features change with time on standing at 20 °K. Finally, some of the absorptions are extremely weak and poorly resolved.

Judgment must be withheld on this evidence for rotation until the data are more secure. Corresponding studies of D_2O and simultaneous studies of the bending region are needed, as well as more evidence on the peculiarities mentioned above.

NH_3 *in* Ar, Xe—Milligan, Hexter and Dressler[29] proposed that NH_3 both inverts and rotates in the matrices nitrogen and argon. However, Pimentel *et al.*[31] showed for nitrogen matrix that aggregation explains the multiplet structure they interpreted. Hanlan[38] continued this investigation of NH_3 with systematic concentration studies using argon and xenon matrices. In each case, the effects of aggregation were clearly noted and, when eliminated, there remained multiplet structures. Thus, Hanlan confirmed the observations of Milligan *et al.* in their argon studies. At this time there seems no question that NH_3 has some sort of librational freedom in argon and in xenon. There remain some difficulties with the detailed interpretation of Milligan *et al.* based on inversion and free rotation: some intensities are not appropriate and temperature dependencies are not completely understood. These factors are still under study.

HCl *in* Ar—A very recent example is provided by the study of HCl in argon by Schoen *et al.*[39] and reported at this meeting. These workers observe a doublet in the spectrum of HCl in argon that shows a temperature dependence which gives convincing evidence for their interpretation that HCl rotates in argon impeded only by a rather low barrier, possibly one near 60 cal. This caused some interest in the Berkeley laboratories because Bulanin[40] had recorded the spectrum of HCl in argon. A comparison of the two spectra revealed the reason. The spectrum recorded by Bulanin contains no evidence of the most intense peak reported by Schoen *et al.* (at 2888 cm^{-1}). The two spectra are contrasted in *Figure 3.*

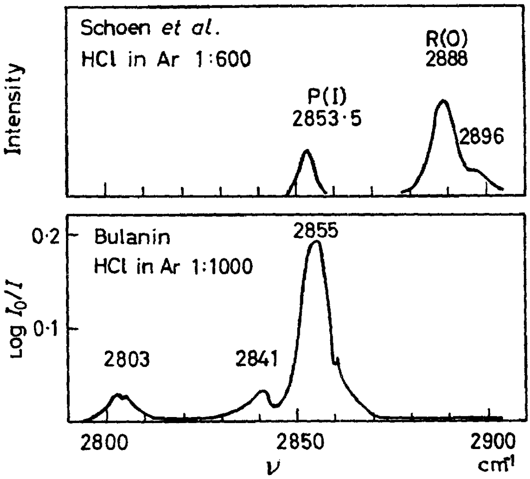

Figure 3. Infra-red spectra of HCl in argon at 20°K
Upper spectrum: Schoen *et al.*, ref. 39
Lower spectrum: Bulanin, ref. 40

Some clue to the explanation of these disconcerting differences was provided by White and Mann in private communication. As they have reported at this meeting, their spectrum, shown in *Figure 3,* does not include all of the features they recorded. These are the only features they recorded that are temperature dependent. In addition they observed, but did not include in their spectrum, perhaps three or four sharp features with seemingly capricious intensity behaviour. Though they always obtained some evidence of the more intense feature at 2888 cm^{-1}, at least their alternate spectrum opens an avenue of explanation for why the Bulanin spectrum omits it completely. Searching for the factor of difference, Bulanin's spectrum was for a sample deposited upon CsI, whereas the Schoen *et al.* spectra were mostly for samples deposited upon sapphire.

Despite these clouds—the difference from the Bulanin spectrum and the capricious bands—the temperature evidence of Schoen *et al.* is convincing and it seems probable that their analysis of rotation with a very small hindering potential is correct.

Summary—It seems clear now that some small molecules do rotate or vibrate in inert gas matrices and that multiplet splittings result. On the other hand, there is not, as yet, such an example known for the nitrogen matrix. The continued exploration of such effects should ultimately be fruitful in terms of intermolecular potential functions.

Multiplet sites

Multiple sites in inert gas matrices were proposed to explain electron spin resonance spectra of hydrogen atoms by Foner and co-workers[41].

Schnepp[42] has presented convincing evidence for multiple sites in inert gas matrices on the basis of electronic spectra of metallic atoms. He made a concerted study of both deposition conditions and concentration, eliminating, apparently, the possibility that aggregation is involved. These pieces of evidence from other spectroscopic techniques provide some background for considering this subject for infrared studies.

CH_2O *in* Argon—Harvey and Ogilvie[43] report spectra of formaldehyde in argon at 4 °K which they regard as evidence for multiple trapping sites. They were concerned about the possibility of aggregation and varied the mole ratio of Ar/CH_2O from below 100 to 300. Their spectra showed triplet features that are quite incompatible with expectations for free rotation. They also argue against restricted rotation and conclude that the three types of sites may be holes of different sizes.

Experience in the Berkeley laboratories would suggest that the possibility of aggregation cannot be ruled out unless concentration studies are extended to much higher mole ratios than 300.

C_2H_6 *in* CF_2Cl_2—Allen, Kennedy, and Pritchard[44] reported what was obviously a frustrating search for CH_3 from pyrolyzed di-t-butyl peroxide. These workers were able to show that the presence of other than matrix molecules in the cage causes changes in the matrix spectrum of ethane. They showed that this is not uncommon. For example, di-t-butyl peroxide added to an ethylene–CF_2Cl_2 mixture altered the spectrum of ethylene. These effects have been noted in the Berkeley laboratories and we concur in their conclusion that incomplete isolation gives noticeable spectral effects though we feel they are unduly pessimistic in their discouraging warning that " it is therefore most unsafe to rely on infrared evidence for the existence of a trapped radical unless simultaneous corroboration is obtained by some other means. . . ."

Summary

On the one hand, this paper shows that there is much to be learned about the effect of matrices upon infrared spectra. Until much more is known, routine use for infrared study of unstable species will be impeded. On the other hand, the large number of studies cited here shows that substantial progress is being made. And, inevitably, the raising of questions opens new lines of thought. Thus the difficulties of interpretation that have frustrated users of the matrix method have added new dimension and new interest to the technique.

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