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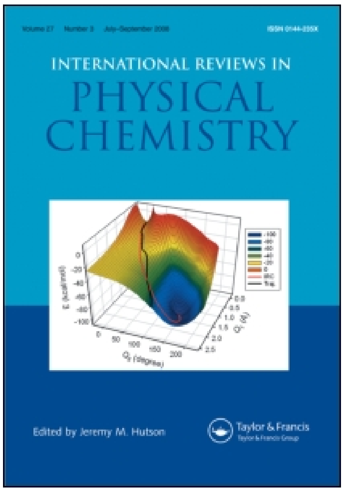

International Reviews in Physical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713724383

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To cite this Article Bishop, David M.(1994) 'Effect of the surroundings on atomic and molecular properties', International Reviews in Physical Chemistry, 13: 1, 21 — 39

To link to this Article: DOI: 10.1080/01442359409353289

URL: http://dx.doi.org/10.1080/01442359409353289

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INTERNATIONAL REVIEWS IN PHYSICAL CHEMISTRY, 1994, VOL. 13, NO. 1, 21–39

Effect of the surroundings on atomic and molecular properties

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This review is concerned with three types of physical phenomena which are affected by the environment of the species under study. They are the vibrational spectrum, nonlinear optical properties, and nuclear magnetic shielding of the molecule (or atom) of interest. The two types of environment discussed are liquid solvents and zeolite cages. The emphasis is on the theoretical–calculational aspects but experimental studies will also be referred to wherever appropriate. The primary objective is to bring under one wing these different phenomena and environments. To give two examples: the methods used to evaluate the vibrational spectrum of a molecule trapped in a zeolite cage should bear some relation to the chemical shift of an atom trapped in the zeolite; the effects of a solvent on a species' nonlinear optical properties (e.g. second harmonic generation) should be understandable in the same way as the effects on the species' vibrational spectrum and magnetic shielding constants. Both perturbation-theoretic and *ab initio* variational methods are employed in describing what has been accomplished and a general, but brief, discussion of how electric fields behave in solutions is given. Most of the calculations reviewed are far from the accuracy of their gas phase counterparts and it is realized that, in the subject of this article, many questions remain unanswered and that there is often little consensus about the best approach to take for the problem at hand. A bringing-together of the topics reviewed may shed some light. The references selected are not exhaustive but it is hoped that they are sufficient to illuminate the author's primary goal.

1. Introduction

The theoretical chemist's perfect system is a simple isolated atom or molecule; however, this situation is seldom, if ever, to be found in nature. Consequently, most chemical reactions and physical measurements are performed in solution or, perhaps, on a species trapped in a solid cage, e.g. a zeolite.

The surroundings necessarily, then, affect the measured property and it is with this fact that the present review is concerned. Three phenomena will be considered (infrared spectra, nonlinear optical processes, and nuclear magnetic shielding) and two types of surroundings (liquid solvent and zeolite cage). These, individually, are subjects which have been studied extensively but there has been little transferrence of information from one phenomenon to another and from one type of surroundings to another. It is the author's hope that what follows will stimulate thinking in this direction.

Two rare examples of the kind of cross-fertilization and unification that are to the point are (*a*) the work of Augspurger *et al.* (1991) on the correlation of ^{13}C and ^{17}O chemical shifts and vibrational frequency of electrically perturbed carbon monoxide, and (*b*) the treatment by Schmeits and Lucas (1976, 1983) of a zeolite α cage as a spherical cavity in a solid which is thought of as a dielectric continuum—something straight out of the theory of liquids. In table 1, the scheme which will be followed for solutions is shown and the same will hold true for zeolites. It should be mentioned right

0144–235X/94 $10·00

away that space will not allow reference to everything that has been done in this area and that the work which is described is simply in order to make the points that lead to a comprehensive view of both properties and surroundings. When a molecule interacts with its surroundings, its physical properties change. Perturbation theory usefully identifies the nature of these changes, see, e.g. Magnasco and McWeeny (1991), as (*a*) electrostatic (or Coulombic), (*b*) induction (or polarization), (*c*) dispersion (or van der Waals interactions), and (*d*) exchange-overlap.

The first accounts for the semiclassical interaction between the rigid charge distributions of the molecule and its surroundings. The second is the change resulting from the distortion of the charge distribution of the molecule by the mean electric field provided by the surroundings. The third describes changes coming from intermolecular correlation due to the instantaneous coupling of the electronic density fluctuations mutually induced in both the molecule and its surroundings. Exchange-overlap effects are of short range and arise from the antisymmetry requirement for the wavefunction. All these effects but the first exist also for atoms. In principle, then, changes brought about by the surroundings should be explainable in terms of these four types of interaction. It should be noted that under (*a*) and (*b*) there will also be an effect from fields emanating from the dipoles induced in liquid surroundings by the solute molecule should it be polar—this is known as the reaction field effect.

In two of the phenomena under review, external fields are involved. This introduces additional considerations. In nonlinear optics the external, macroscopic, Maxwell electric field is altered by its passage through the medium and this change is reflected, as we will see, by the incorporation of 'local field factors'. Similarly, in liquid magnetic shielding experiments, the external magnetic field induces in the medium a diamagnetic polarization which, generally, increases the magnetic field experienced by the solute; this is called the bulk susceptibility contribution and, since it depends on the shape of the sample, it can usually be extracted from the experimental data. There is also present in such experiments, a neighbour-molecule magnetic anisotropy contribution produced by local magnetic fields caused by anisotropy in the magnetizability of the neighbouring molecules.

To return to our theme, what connections can we make within this framework? Clearly, whether we are talking about surroundings which are essentially atoms or ions, as in a cage, or solvent molecules, as in a solution, these four contributions all, to a greater or lesser extent, exist even though the distances between the molecule (atom) and its neighbours may differ. In both cases we may choose to ignore one or more of these contributions, e.g. very often the short-range (repulsive) exchange-overlap effects can be neglected. Further, when it comes to changes brought about by an electric field (external or internal) or a magnetic field, Buckingham (1967) has shown that the changes to a property may be expressed by a Taylor series in the field and the coefficients in the series (dipole polarizability, hyperpolarizability, shielding polarizability, etc.) are intrinsic to the atom or molecule of interest.

Table 1. Scheme.

Phenomenon	Measurement	Comment
Infrared spectrum	frequency shift	no external field
Nonlinear optics	hyperpolarizabilities	external electric field
Magnetic shielding	medium shift	external magnetic field

When we turn to a more quantitative analysis, we find that, computationally, the usual strategy of a variational calculation involving all species of interest is not feasible, though there are research programmes with this as their objective. Even with today's computers this 'supermolecule' approach is very expensive.

It has therefore been customary to use perturbation theory both for analysis and as a working tool. By this, is included those calculations that simulate the surroundings by a continuous dielectric medium (thereby reducing the system to an effective two-body one) and those that consider the interaction between a solute species and one neighbour (pair theory) and then use a statistical approach to incorporate all neighbours.

The part of this review concerning solutions follows the order in table 1 and the same order is taken for zeolite cages. It is hoped that, by bringing together in one article these separate systems and phenomena, an understanding will develop which will lead to further progress on all fronts. A prelude to this review is the article by Buckingham which was published in 1980.

2. Solutions

Since some of the experiments which will be described involve an external electric field, we will start this section with some broad concepts concerning dielectric polarization; this, incidentally, will introduce the concept of a reaction field, an idea which has frequently been used in the computation of solvent effects where no external field is present. Two useful books are those by Böttcher (1973) and Rummens (1975) and three important reviews have been written by Buckingham (1972), Tapia (1982) and Ángyán (1992).

The concept of dielectric polarization goes back to the days of Cavendish and Faraday but it was only at the beginning of this century that Debye (1929), Bell (1931), Onsager (1936) and Kirkwood (1939) laid the foundations of the theory which still holds sway today. In this theory one considers the species of interest (solute) to be embedded in a cavity of a continuous dielectric (solvent). The shape of the cavity and the charges on its surface have been the subject of much discussion and we will return to these topics later. Two defects of the continuum model which have not received due attention, however, are the discontinuity at the cavity–dielectric interface and the assumption that the first solvent shell has the same properties as the bulk solvent.

In a solution in an external electric field (E), the electric field in the cavity is modified in two ways—both leading to an increase in its magnitude. The first comes from simple electrostatics and gives the field in a spherical cavity of dielectric ϵ as

$$E_c = [3\epsilon/(2\epsilon+1)]E. \tag{1}$$

However, in homogeneously polarized matter we have what Böttcher calls a virtual spherical cavity and the cavity field should be increased by the apparent charges on the cavity boundary:

$$E_v = E_c + E_{sph}. \tag{2}$$

Determination of E_{sph} leads to

$$E_v = (1 - g\alpha)^{-1} E_c, \tag{3}$$

where g is the reaction field factor and is defined by

$$g = [2(\epsilon-1)/(2\epsilon+1)]a^{-3}/(4\pi\epsilon_0), \tag{4}$$

where a is the radius of the cavity and α is the polarizability of the liquid (SI units are employed). One way, there are several, of determining a is through Onsager's relation:

$$(4\pi/3)(N/V)a^3 = 1, \tag{5}$$

where N/V is the number of particles per unit volume. We note that other choices will lead to different results for g and likewise for the internal field. Differences will also occur if we use a non-spherical cavity. If the liquid is non-polar, then

$$(4\pi/3)(N/V)\alpha = (\epsilon - 1)/(\epsilon + 2), \tag{6}$$

and if it is polar, then

$$(4\pi/3)(N/V)\alpha = (\epsilon_\infty - 1)/(\epsilon_\infty + 2), \tag{7}$$

where ϵ_∞ is the dielectric constant in a high-frequency oscillating electric field. The reason for the distinction between equations (6) and (7) is that for a polar liquid the dielectric constant (ϵ) has an orientational contribution, as discovered by Debye, and, to obtain the polarizability, this contribution must be excluded; using a high-frequency field has the effect of doing this. Combining these equations leads to

$$E_v = [(\epsilon + 2)/3]E, \tag{8}$$

for a pure non-polar liquid, and

$$E_v = [\epsilon(\epsilon_\infty + 2)/(\epsilon_\infty + 2\epsilon)]E, \tag{9}$$

for a pure polar liquid. These two relations, coupled with the Maxwell relation linking ϵ with the refractive index (n)

$$\epsilon = n^2, \tag{10}$$

will be used later to define the local field factor used in nonlinear optical experiments. Furthermore, the field factor (g) in equation (4) will be invoked in determining the reaction field induced on a cavity surface by a polar solute, which in turn will interact with the solute's dipole moment giving an electrostatic-inductive solvent effect. This should not be confused with the use of g in finding the magnitude of an external field inside a cavity.

Now let us consider, using perturbation theory, the general form for the change in vibrational energy of a species in a solvent and which is needed for a discussion of infrared spectra in solutions. This was worked out many years ago by Buckingham (1958, 1960a, b). He supposed that the relevant interaction energy from solvent effects, to be incorporated in the Hamiltonian of the solute, could be expressed as a Taylor series in the normal coordinates Q_n:

$$U = U_e + \sum_n U'_n Q_n + \frac{1}{2}\sum_{n,m} U''_{nm} Q_n Q_m + \dots, \tag{11}$$

where $U'_n = (\partial U/\partial Q_n)_e$, and that the potential function could similarly be expressed by

$$V = V_e + \frac{1}{2}\sum_n \omega_n^2 Q_n^2 + \frac{1}{6}\sum_{k,l,m} f_{klm} Q_k Q_l Q_m + \dots . \tag{12}$$

Considering only the lowest-order terms, the shift in the fundamental vibrational frequencies is (Buckingham (1960b), equation (24), though using a slightly different notation)

$$\begin{aligned} \Delta(\hbar\omega_n) &= E_n - E_0 \\ &= (\hbar/2\omega_n)(U''_{nn} - \sum_a f_{ann} U'_a \omega_a^{-2}), \end{aligned} \tag{13}$$

where f_{ann} are the anharmonic cubic force constants. This equation was recently, unknowingly, re-derived by Bishop (1993) and it is equivalent to simple vibrational averaging to first order in the quadratic and cubic terms in equations (11) and (12), respectively. Every fundamental vibrational energy level is shifted by

$$U_e - \tfrac{1}{2}(U'_n)^2\omega_n^{-2} + (n+\tfrac{1}{2})\Delta(\hbar\omega_n). \tag{14}$$

The first two terms cancel when finding a fundamental transition energy. Buckingham then introduced simple reaction field theory to account for the interaction energy between solute and solvent. That is, the solvent produces a field proportional to the dipole moment (μ) of the solute ($\mu \neq 0$ since we are witnessing infrared spectra):

$$F = g\mu, \tag{15}$$

where g is defined by equation (4). This field then interacts with μ, leading to the new interaction energy:

$$U = U_e - \tfrac{1}{2}g\mu^2(1-g\alpha)^{-1}, \tag{16}$$

for a non-polar solvent. Equation (16) together with equation (4) allows U'_n etc. to be found and together with the spectroscopic constants and equation (13) gives a recipe for obtaining the solvent shifts of the fundamental frequencies. If used, and the author is not aware that they have been, these equations offer an approximate check on alternative computations of solvent shifts in infrared spectra.

Because of its beguiling simplicity, the reaction field concept has been much more widely used than just for solvent effects on vibrational spectra. But it should be recognized, see the previous section, that it takes care, at the most, of only the electrostatic-inductive contribution to the solute–solvent interaction. It has recently been introduced into the Gaussian set of programmes and hence it will undoubtedly be very much used in the future (perhaps, sometimes unwisely). The incorporation of this particular solvent effect as a perturbation to the Hartree–Fock equations, which are the basis of the most frequently employed *ab initio* procedures, has been put to great advantage by Wiberg and co-workers (Wong *et al.* 1991a), with the calculation of a broad range of properties. Significantly, in their application, the reaction field is used self-consistently, that is to say, the induced dipole moment is allowed to change the reaction field and thus an iterative procedure is implemented. This is an improvement over the non-self-consistent procedure of Rivail and Rinaldi (1976). Wiberg's group obtain, analytically, the second and third derivatives of the Hartree–Fock energy, leading directly to predictions of the infrared spectrum. Further, they optimize the geometry of the solute in the presence of the reaction field and ensure that the centres of cavity and electronic distribution coincide. They maintain that this model (called the self consistent reaction field (SCRF) model) has been successful in the calculation of conformational energies, isomerization energies and electronic spectra.

The use of the cavity reaction field model has not been restricted to *ab initio* calculations, e.g., Fox and Rösch (1992), Fox *et al.* (1993), have employed it in incomplete neglect of differential overlap (INDO) calculations as have Karelson and Zerner (1990).

Of great interest in the implementation of this method, has been the shape and size of the cavity. Wiberg's group uses either the molar volume (the original Onsager paradigm) or they compute the 0·001 a.u. electronic density envelope of the solute and scale it by 1·33. In both cases they add 0·5 Å to account for nearest approach of solvent molecules. Olivares del Valle *et al.* (1993) have argued that the size of the cavity should be related to the charges on the solute and be determined self-consistently. Fox and Rösch (1992), Fox *et al.* (1993) have considered arbitrary shapes made up of curved triangles with a distribution of charges on each triangle which are determined self-consistently. Rivail *et al.* (1985) have concluded that an ellipsoid (defined by a constant potential surface), determined self-consistently, is superior to a sphere; further, Rinaldi *et al.* (1983) have suggested that the ellipsoidal axes should be proportional to the cube root of the principal axes of the dipole polarizability tensor. Rivail's group (Dillett *et al.* 1993) have also proposed a general algorithm for the computation of reaction field factors for a distributed multipole analysis of the charge distribution of the solute. Finally, Tapia and Goscinski (1975) have carried out model self-consistent calculations using g as a parameter. It would appear that cavity questions will be a fruitful area for model building for quite some time.

2.1. *Vibrational spectroscopy*

Many of the general ideas of how to treat solvent effects, as just outlined, have been utilized in the investigation of a variety of spectroscopic processes, e.g., the solvatochromic effect in electronic spectroscopy (Karelson and Zerner 1990). Here, we shall concentrate on one aspect: the change in vibrational frequencies and intensities of a solute molecule embedded in a solvent. We make this choice since there is a parallel with similar work on molecules trapped in zeolites (§ 3.1).

Wiberg and co-workers (Wong *et al.* 1991b) have carried out a calculation of the frequency and intensity shifts for a formaldehyde molecule placed in acetonitrile. The simple spherical-cavity-in-a-dielectric-continuum model was used, with the cavity centre at the centre of the electronic distribution of the system. The reaction field induced by the effect of the solute on the solvent was incorporated in the usual SCF treatment which included the determination of first and second derivatives of the Hartree–Fock energy and the derivative of the dipole moment with respect to the normal coordinates (required for the intensity calculations). The cavity size was found in the two ways mentioned previously. The authors state that their results are similar in either case. There was also a study made of the basis set size and the treatment included geometry optimization for the solute. The frequency shifts were in good agreement with experiment but there were no experimental intensities with which to compare. In the same paper they looked at the stretching-frequency shifts of the carbonyl group in a variety of compounds with both acetonitrile and cyclohexane as solvents; again, with good results. There were, however, significant differences between the theoretical and experimental absolute intensities, though the *ratios* of the intensities observed in gas and liquid were satisfactorily reproduced by the theory. In a later paper by the same authors (Wong *et al.* 1992), electron correlation, through second-order Møller–Plesset (MP2) theory, was included in a study on sulphamic acid. Once more, a spherical cavity was used and the radius was based on the molar volume of the crystal, augmented by 0·5 Å. In a medium of dielectric constant $\epsilon = 40$, large frequency shifts ($> 50\,\mathrm{cm}^{-1}$) were found. A comparison of the gas-phase calculated values with the frequencies observed in the solid state, showed a considerable improvement when solvent effects were included. One should comment that the choice of highly polar solvents will favour the self-consistent reaction field (SCRF) method, since electrostatic-inductive effects will then dominate. By the very nature of the model (a dielectric continuum) there are no dispersive, or repulsive effects. Also, some of the success must be attributed to the incorporation of semi-adjustable parameters such as cavity size. It should be borne in mind that the perturbation to the solute Hamiltonian excludes higher-order terms such as αF^2 and $\theta F'$, where α is the dipole polarizability, θ the quadrupole moment and F' the field gradient. On the positive side, the allowance for geometry optimization of the solute (though not of the solvent) brings the theoretical model closer to reality; as does the introduction of self-consistency between the solute's dipole moment and the reaction field.

Rivail and Rinaldi (1976) have also considered a molecule in a spherical cavity in a dielectric continuum, but rather than use the conventional g reaction-field-factor, they use a multipolar expansion of the interaction energy between solute and solvent. This they incorporate in the SCF equations which are solved by semi-empirical means, initially complete neglect of differential overlap (CNDO) and later modified neglect of diatomic overlap (MNDO) (Rinaldi *et al.* 1986). In the latter work they calculated the vibrational polarizability (Bishop 1990) of 1-2 difluoroethane which is directly related to the infrared intensity (Bishop and Cheung 1982) when the double harmonic oscillator approximation is invoked. These were model calculations with a solvent of $\epsilon = 10$ and no comparison with experiment was made.

A quite different approach to the SCRF one, is that of Linder (1992). His is based on perturbation theory and accounts for dispersion as well as electrostatic and inductive interactions. It still retains the continuous dielectric model but relates the solvation effects on infrared intensities to the moments and polarizabilities (and their derivatives) of the solute and to ϵ and ϵ_∞ of the solvent. In the example he gave, LiH in tetrahydrofuran (chosen since the needed properties of LiH were available—Bishop and Lam 1985), he found that dispersion was the dominant contributor. He found a very strong solvation effect on the intensity but since no infrared intensity measurements are available for LiH solutions, his results remain predictions. The method's reliance on knowledge of the polarizability and hyperpolarizability (frequency-dependent values would be even better) of the solute, means that until more of these optical properties are known, further exploitation of this method will be limited.

2.2. *Nonlinear optics*

The field of nonlinear optics has expanded greatly in the last decade and become an important part of materials science. This is not the place to give a formal review of these advances from a theoretical standpoint; there are several which already exist (Buckingham 1967, Bogaard and Orr 1975, Bishop 1994, Shelton and Rice 1994). Our interest is strictly in solvent effects. It should be noted that theory has been able to match, to a high degree of accuracy, nonlinear optical experiments carried out in the dilute gas phase. However, computational procedures for the liquid phase are still in their infancy. In simplistic terms, the experiments are related to the frequency-dependent hyperpolarizabilities (β, γ, etc.) which are intrinsic molecular properties and can be thought of as higher-order polarizabilities, i.e. a measure of the effect of an electric field on the dipole polarizability (α). The reader should be warned of two rather mundane but nevertheless important points: (*a*) not all theoreticians use the same definition of β and γ, they may differ by a numerical factor, and (*b*) not all experimentalists use the same quartz standard for measuring the required quantities. Fortunately, these traps have been recognized and elucidated by Willetts *et al.* (1992) and anyone interested in this field should read this paper.

The significant difference between the infrared phenomena, described in the previous section, and nonlinear optical processes is that in the latter there is an external electric field present. This means that the solvent does two things, which must not be confused: one, it changes the field(s) which are experienced by the solute and, two, it changes the geometry and electronic distribution of the solute from what it is in the dilute gas phase to what the internal electric field actually sees. So that, though, in the gas phase any external electric field can be, more or less, taken at face value and the gas molecule (atom) can be assumed to be in its natural unperturbed state, this cannot be assumed in a solution. Therefore, in comparing experiment with theory for solutions, there will be two corrections to be made. The first has long been known to experimentalists and taken care of by the introduction of local field factors. The second has only recently gained the attention of theorists.

The actual field at the site of a solute particle in a solution is a problem we have already encountered; see equations (8)–(10). These equations are the basis of most discussions of local field factors: see Levine and Bethea (1975) and Singer and Garito (1981). For pure polar liquids, the field factor (i.e. the number multiplying the actual field to get the internal field) is

$$f_0=\epsilon(\epsilon_\infty+2)/(\epsilon_\infty+2\epsilon), \tag{17}$$

and, if the field oscillates with a frequency ω, then

$$f_\omega=\epsilon_\omega(\epsilon_\infty+2)/(\epsilon_\infty+2\epsilon_\omega). \tag{18}$$

Usually the approximation $\epsilon_\omega \cong \epsilon_\infty \cong n_\omega^2$, where n_ω is the refractive index at frequency ω, is made and this leads to

$$f_\omega=(n_\omega^2+2)/3, \tag{19}$$

and

$$f_0=\epsilon(n_\omega^2+2)/(n_\omega^2+2\epsilon). \tag{20}$$

All the strictures that have been passed previously on the spherical-cavity-continuum-model will also apply to these equations.

Now let us turn to the effects that the solvent has directly on the solute with respect to its nonlinear optical properties. Teng and Garito (1983) quote a good example: after local field effects are taken into account, the mean hyperpolarizability β of *para*-nitroaniline (PNA) in *trans*-stilbene is $6{\cdot}4\times10^{-30}$ esu (Levine and Bethea, 1978) and in methanol is $34{\cdot}5\times10^{-30}$ esu (Oudar and Chemla 1977). Teng and Garito carried out calculations for β for PNA using a sum-over-states formula requiring electronic transition dipole moments and energies. These were obtained by an SCF configuration-interaction technique. In the solvents the required transition energies were shifted and the following equation was used:

$$\hbar\Delta\omega_{ng}=A(\mu_n-\mu_g)(\mu_n+\mu_g)+B(\mu_n-\mu_g)\mu_g, \tag{21}$$

where

$$A=[(n^2-1)/(n^2+1)]a^{-3}/(4\pi\epsilon_0),$$

$$B=2[(\epsilon-1)/(2\epsilon+1)-(n^2-1)/(2n^2+1)]a^{-3}/(4\pi\epsilon_0),$$

with n the refractive index, ϵ the dielectric constant of the solution, a the cavity radius, and μ_n and μ_g the solute dipole moments for the excited and ground states, respectively. The first term is the reaction field experienced by the permanent dipole moment of the solute on its interaction with the induced dipole moments of the surrounding molecules. The second term is the interaction with the permanent dipole moments of the surrounding molecules. Equations (22) and (23) are clearly based on the spherical cavity model. Within experimental error, the agreement between theory and experiment was found to be satisfactory for both PNA and 2-methyl-4-nitroaniline in dioxane.

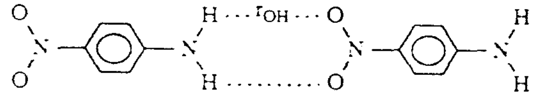
Stähelin *et al.* (1993) have compared the measured gas and liquid phase values of $\langle\gamma\rangle$, the macroscopic hyperpolarizability in a second-harmonic-generation experiment, for acetonitrile. There is a factor of 13 between the two measurements and local field factors account for only 2·9 of this. The authors seem to imply that direct solute–solvent interactions should be included in the local field factors. The present writer is not of this opinion but rather that local field factors should be associated only with the enlargement of the external field(s) by the solvent and the other changes should be represented as a correction to the property due to a change in its electronic distribution.

Willetts and Rice (1993) seem to continue this misunderstanding by calculating $\langle\gamma\rangle$ for liquid acetonitrile and then comparing their values with the experimental ones which still contain the local field factors. Their method is similar to the one of Wiberg and co-workers (see § 2.1) except that there is no self-consistency maintained between the reaction field and the solute's dipole moment. In this sense the method is more akin to that of Tapia and Goscinski (1975). Both SCF and MP2 (Møller-Plesset second-order theory) calculations were performed with the usual reaction field providing an additional term to the Fock matrix elements:

$$F_{\lambda\sigma} = F^0_{\lambda\sigma} + g\mu\langle\lambda|\hat{\mu}|\sigma\rangle. \tag{22}$$

In addition to using a spherical cavity, they also explored the use of an ellipsoidal one. Their results, however, were not definitive since widely differing numbers could be obtained by changing the cavity size. As well, the experimental values had extremely large uncertainties. The authors concluded that more sophisticated models were required. One drawback to the model they chose is that it is inapplicable to non-polar liquids. Finally, one wonders if the change in the β hyperpolarizability could not be simply expressed in terms of the next higher-order hyperpolarizability γ, i.e. $\Delta\beta = \gamma g\mu$, at least as far as inductive effects are concerned.

The last three papers to be reviewed all concern PNA. Stähelin *et al.* (1992) have measured β for this molecule in a number of solvents with results ranging from 8·1 to $15{\cdot}8 \times 10^{-30}$ esu. A plot of β against $\lambda_{\max}$ (the charge transfer absorption maximum) shows a proportionality to the 5·4 power of $\lambda_{\max}$ rather than the quadratic dependence which would be found in a simple two-state model. A four-level Hückel model was used to explain this result. Luo *et al.* (1993) do take a two-state sum-over-states model for β for PNA and use the experimental electronic excitation energy from solution studies and the required dipole transition moments from a multiconfigurational quadratic response calculation. This technique, however, accounts for only half of the solvent (dioxane) effect on β. They concluded that solvent changes to the dipole transition moments must also be significant. This would appear to be in conflict with the results of Teng and Garito (1983). Finally, of relevance to these calculations is the semi-empirical work, Hartree–Fock Austin Model One (AMI), of Yasukawa *et al.* (1990) on the PNA dimer



For $r_{O\text{–}H} = 2{\cdot}25$ Å, they found that β is three times larger per PNA monomer than for the isolated monomer and that this is due to π–π interactions rather than electrostatic interactions or H bonding. This shows that any definitive work on the hyperpolarizabilities of PNA in the liquid phase will have to go beyond simple reaction field models.

2.3. *Nuclear magnetic shielding*

There has been less recent interest in solvent effects on nuclear magnetic shielding than for the two previous topics. One might have thought that the SCRF computational approach would have been tried out, but this has not been the case. Instead most theories have been based on rather simple models for the interaction between a single solute and a single solvent molecule (or atom) coupled with some form of statistical averaging. A useful book dealing with these theories is that by Rummens (1975) and also reviews by Jameson (1980, 1991).

The standard procedure is to write the change to the magnetic shielding caused by the solvent as

$$\Delta\sigma=\sigma_b+\sigma_a+\sigma_e+\sigma_w+\sigma_r, \tag{23}$$

(Buckingham *et al.* 1960) where σ_b accounts for the induced diamagnetic polarization produced by the external magnetic field, it is known as the bulk susceptibility effect and depends on the shape of the sample tube and the direction of the applied field; it is proportional to the molar magnetic susceptibility. σ_a, known as the neighbour-molecule magnetic anisotropy effect, is produced by the magnetizability anisotropy in the neighbouring solvent molecules and was first investigated by Stephen (1958). Of more immediate interest to us are the next two terms; because of the distances involved, the repulsion term σ_r is usually ignored. σ_e accounts for changes occurring through the electric field generated by the surrounding molecules and hence distortion of the solute by polarization. σ_w accounts for changes due to van der Waals interactions and is always present.

In the original treatment (Raynes *et al.* 1962) σ_e and σ_w were first evaluated for a pair of molecules giving $(\sigma_{\text{pair}})_e$ and $(\sigma_{\text{pair}})_w$ and then the expression.

$$\sigma_1=\tfrac{1}{2}N\int\sigma_{\text{pair}}\exp(-u/kT)\,d\tau \tag{24}$$

was used for the overall shift, where: σ_1 is the coefficient of the reciprocal of the molar volume (V_m) in a power series expansion of σ_m in V_m, N is the Avogadro constant, u is the intermolecular potential function and τ symbolizes the mutual orientation and distance between the interacting species. Originally, u was represented by the Stockmayer potential (an elaboration of the Lennard–Jones 6–12 potential). With particular forms for $(\sigma_{\text{pair}})_e$ and $(\sigma_{\text{pair}})_w$, the integration in equation (24) could be carried out analytically.

When a molecule is placed in a *uniform* electric field (F), the shielding can be expressed, using standard tensor notation by (Buckingham 1960c):

$$\boldsymbol{\sigma}_{\alpha\beta}=\boldsymbol{\sigma}^0_{\alpha\beta}+\boldsymbol{\sigma}_{\alpha\beta\gamma}F_\gamma+\tfrac{1}{2}\boldsymbol{\sigma}_{\alpha\beta\gamma\delta}F_\gamma F_\delta+\dots, \tag{25}$$

and $\boldsymbol{\sigma}_{\alpha\beta\gamma}$, $\boldsymbol{\sigma}_{\alpha\beta\gamma\delta}$ are known as the shielding polarizabilities. Averaging these quantities over all directions of the magnetic field but with the electric field held fixed, gives the mean shielding polarizabilities A, $B_\parallel$ and $B_\perp$ and the expression

$$(\sigma_{\text{pair}})_e=-AF_\parallel-B_\parallel F_\parallel^2-B_\perp F_\perp^2, \tag{26}$$

where $F_\parallel$ and $F_\perp$ are fields parallel and perpendicular to the axis of symmetry; the expression applies to axially symmetric systems (Raynes and Ratcliffe 1979).

The field F is regarded as having three sources: (*a*) the electric dipole moment of the perturbing molecule, (*b*) the electric quadrupole moment of the perturbing molecule, (*c*) the electric dipole moment in the perturbing molecule induced by the permanent dipole moment of the solute molecule (shades of reaction field theory). Though initially it was assumed that the polarizability of the perturber was isotropic, this restriction has been dropped by Raynes (1993) in a more recent formulation.

The van der Waals contribution is written as

$$(\sigma_{\text{pair}})_{\text{w}} = -B\overline{F^2}, \tag{27}$$

where F is a fluctuating field due to dispersive attractive forces. Though F averages to zero, its mean square does not. In Raynes *et al.* (1962) an approximate quantum-mechanical treatment led to

$$\overline{F^2} = 3\alpha I r^{-6}/(4\pi\epsilon_0)^2, \tag{28}$$

where α and I are the polarizability and ionization potential of the perturbing molecule and r is the distance between the interacting pair, SI units being employed.

Since σ_{w} is the only contribution for atoms and even for molecules it is often the dominant quantity; there have been many other schemes for its evaluation (Rummens 1975). Howard *et al.* (1962) considered infinitely-dilute solutions of non-polar molecules in non-electrolytes and treated the effects of dispersion with the continuum model. They deduced that the dispersion contribution to the free energy of a pure substance is:

$$E_{\text{dis}} = -\tfrac{1}{8}\langle m^2\rangle g, \tag{29}$$

where $\langle m^2\rangle$ is the averaged square of the oscillating dipole moment of the free molecule, or, for a mixture

$$E_{\text{dis}} = -\tfrac{1}{4}\langle m^2\rangle g[\nu_1/(\nu_1+\nu_2)], \tag{30}$$

where ν_1 and ν_2 are the mean absorption frequencies of solvent and solute, respectively. Combining this equation with

$$E_{\text{dis}} = -\tfrac{1}{2}\alpha_2\overline{F^2}, \tag{31}$$

and

$$\langle m^2\rangle = \tfrac{3}{2}h\nu_2\alpha_2, \tag{32}$$

gave

$$\overline{F^2} = \tfrac{3}{4}hg[\nu_1\nu_2/(\nu_1+\nu_2)]. \tag{33}$$

Equations (27) and (33) then produce σ_{w} directly, no statistical averaging being required since the pair is now simply the solute and the dielectric continuum.

In another theory (Kromhout and Linder 1969), which concerned the dispersion effect on closed shell atoms, triple perturbation theory was used to determine the effect of a single perturber at a fixed separation and the solvent shift due to the medium was obtained statistically. After a number of approximations, Kromhout and Linder found:

$$\sigma_{\text{w}} = -4\pi\frac{N}{V}U_2\frac{(3U_1+2U_2)}{(U_1+U_2)^2}\alpha_1\alpha_2\sigma_0 d_0^{-3}C/(4\pi\epsilon_0)^2, \tag{34}$$

where U_1 and U_2 are effective excitation energies, d_0 is the Lennard-Jones collision diameter and C is a function of the expectation values of various powers of the electronic coordinate r. The contribution for a single pair was:

$$(\sigma_{\text{pair}})_{\text{w}} = \sigma_0 W\left[\frac{3U_1+2U_2}{U_1(U_1+U_2)}\right]C, \tag{35}$$

where W is the van der Waals energy. We notice that in this theory there is no separation into the shielding polarizability and an effective $\overline{F^2}$.

There has been little consensus as to which of the above theories is the most appropriate; this is largely due to lack of knowledge of the effect of an electric field on nuclear magnetic shielding (as characterized by the shielding polarizabilities). Since the approximate calculation of B for the noble gases by Jameson *et al.* (1970) (A is zero for an atom), there has been the work of Raynes and co-workers (e.g. Packer and Raynes 1990, Grayson and Raynes 1994, Dykstra and co-workers (e.g. Augspurger and Dykstra 1991), and Bishop and Cybulski (1993a, b, 1994). As more data on shielding polarizabilities is becoming available, it is apparent that some of the theories of the sixties and seventies are inadequate. A good example of this is the comparison of the values of B for the noble gases. Seydoux *et al.* (1993) have measured gas–liquid σ shifts for He, Ne, Kr, and Xe. Using effective values of $\overline{F^2}$ given by the above-mentioned theories, they have extracted values of B. In all cases these values were vastly larger than those found by *ab initio* calculations (Bishop and Cubulski 1993b, 1994). Raynes has observed the same dilemma for calculated and measured ^{1}H and ^{13}C shielding shifts (σ_w) in methane (Raynes 1993).

Most likely these problems will be resolved by making *ab initio* calculations of σ for pairs of molecules and then introducing some form of statistical averaging. Jameson and de Dios (1992) have made a start in this direction. In the meantime, SCRF calculations on magnetic shieldings, even though they ignore dispersion, may turn up some interesting ideas.

As a final comment, values of the shielding polarizabilities will allow the σ_e term in equation (23) to be found, if the field strength is known, and therefore, by elimination the value of the van der Waals shift σ_w.

3. Zeolites

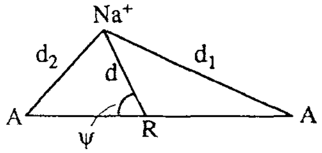
At first sight, a species surrounded by a zeolite cage (oxygen, silicon, aluminium, alkali, and alkaline earth ions) would seem to be a far cry from one embedded in a solution. Yet, they are both quantum mechanical systems and should, in principle, both be able to be tackled in the same way. At the very least, the zeolite produces an electric field and this part of its interaction with a trapped species should involve the dipole polarizabilities, shielding polarizabilities, etc. of the latter, depending on the experiment at hand. Vibrational frequency shifts should, for example, in part, be related to the vibrational Stark effect. An added incentive, not usually explored in solution work, is the information which is gained about the surroundings themselves. However, in spite of the evident importance of zeolites industrially, far less theoretical research has been done on changes to the properties of the species which they entrap. What has been done for infrared spectra, nonlinear optics, and magnetic shielding is reviewed in the following sections.

3.1. *Infrared spectroscopy*

The primary work in this field, both theoretically and experimentally, has been performed by Cohen de Lara and her co-workers. We will only be concerned with the theoretical aspects of their work.

One starting point is to represent the zeolite cage by a number of point charges. In the Na*A* zeolite there are twenty six unit cells surrounding a cavity with 12 Na$^+$ in three different crystallographic sites: eight Na$_{\text{I}}$ in S$_{\text{I}}$, three Na$_{\text{II}}$ in S$_{\text{II}}$, and one Na$_{\text{III}}$ in S$_{\text{III}}$. Barrachin and Cohen de Lara (1986) have discussed two models for Na*A*; in one model they distributed the negative charges of the AlO_4 and SiO_4 tetrahedra on the oxygens and therefore considered only the oxygens (charge $-\frac{1}{4}$) and the cations of the framework. In the other model, they gave silicon, aluminium, and oxygen their full charges ($+4$, $+3$, -2). They found that the first model was satisfactory for evaluating the field at distances from the cavity walls where the trapped species is located. By measuring the infrared intensity of N_2 trapped in Na*A*, they were able to deduce that the field experienced by N_2 is $1{\cdot}7\times10^5$ esu (we will shortly discuss the relation between intensity and field strength). For N_2 aligned towards the most attractive cation (Na_{III}), the field experienced from the point charge model (the first one) is $4{\cdot}3\times10^5$ esu. The authors therefore concluded that the ionic model only gives an estimate of the order of magnitude of the field. Nonetheless, it has continued to be used, see, for example, the approximate *ab initio* calculations (using the self-consistent charge Xα model) of Zakharieva-Pencheva *et al.* (1985).

In two papers (1981, 1989) Cohen de Lara measured and calculated the vibrational frequency shifts of H_2, D_2, N_2, and O_2 absorbed in the Na*A* zeolite. In order to simplify the calculations, she considered the cage perturbation to emanate solely from the Na_{III} ion, even though this is, to a degree, in contradiction to the conclusions of the previously-noted model calculations. With the geometry chosen in the figure below the interaction energy was expressed as



$$U=\tfrac{1}{2}\theta(q/d^3)(3\cos^2\psi-1)/(4\pi\epsilon_0)-\tfrac{1}{2}(q^2/d^4)[\bar{\alpha}+\Delta\alpha(3\cos^2\psi-1)]/(4\pi\epsilon_0)^2$$
$$+A(d_1^{-6}+d_2^{-6})+B(d_1^{-12}+d_2^{-12}), \qquad (36)$$

where q is the charge on Na^+, and θ, $\bar{\alpha}$, and $\Delta\alpha$ are the quadrupole moment, isotropic and anisotropic polarizabilities, respectively, of the diatomic molecule. A and B are dispersive and repulsive constants of the Na^+–A_2 pair. The four parts of equation (36) contribute the electrostatic, inductive, dispersive, and repulsive parts of the interaction.

This interaction potential was then combined with Buckingham's formula, equation (13), as simplified for a diatomic, to produce an expression for $\Delta\omega$ in terms of the derivatives of the molecular properties in equation (36). It may be noted that the inductive component (equivalent to the vibrational Stark effect) is the same as that derived by Bishop (1993); see also Martí and Bishop (1993). Since any distortion of the geometry of A_2 by Na^+, effects the ground state and fundamental state energies equally, $\Delta\omega$ is independent of such effects and the internuclear separation need not be optimized. Many of the required molecular-property derivatives could only be estimated, so that the final values were somewhat crude: for H_2 $\Delta\omega=-199\,cm^{-1}$ (experimental $=-83\,cm^{-1}$) for the minimum-energy configuration of Na^+ perpendicular to H_2; for N_2 $\Delta\omega=+19\,cm^{-1}$ (experimental $=8\,cm^{-1}$) for Na^+ in line with N_2. It may be surmized that this sign change occurs because the $\frac{1}{2}\theta(q/d^3)(3\cos^2\psi-1)$ term changes sign in the two minimum-energy configurations. In order to avoid the problem of using poorly-known properties in this scheme, an alternative approach would be able to carry out a full-scale *ab initio* calculation on the Na^+–A_2 system for different configurations and then determine U' and U'' numerically. Equation (13) could then be used to obtain the final values of $\Delta\omega$.

Cohen de Lara's group has also calculated $\Delta\omega$ for CO_2 and CH_4, though here they have only taken into account the electrostatic-inductive component (dispersive, and repulsive effects were ignored). This makes the theory similar to that of the vibrational Stark effect but with the neglect of anharmonicity. Furthermore, they do not take a value of the internal electric field (F) which is directly related to the zeolite but rather keep this as a parameter, giving values of $\Delta\omega$ for different values of F. For CO_2 (Goulay *et al.* 1991) they get results, using reasonable values of F for Na*A* and Co*A*, which are in severe disagreement with the experimental $\Delta\omega$ values. This doubtless comes from the simplifications in the model coupled with a lack of consideration of anharmonicity. The CH_4 study (Kahn *et al.* 1985) is not really a calculation of $\Delta\omega$ but rather a fit of the parallel and perpendicular second derivatives of the CH bond polarizability (these enter the theory which is the same as that used for CO_2). The fit is made so as to achieve the experimental splitting of the ν_3 frequency. Again, *ab initio* calculations of the interactive energy or of the missing parameters in the model would be in order before a true assessment of this work can be made.

The same group has also investigated the intensity shifts of zeolite-trapped N_2 (Cohen de Lara and Delaval 1978) and CH_4 (Cohen de Lara *et al.* 1992, Soussen-Jacob *et al.* 1992). In both cases model calculations were carried out in order to determine the effective fields in the cavity; for CH_4 the C_3 axis was aligned with the field in the Na_{III} direction, for N_2 several orientations were looked at, but the alignment of the nuclear axis with the Na_{III} ion was preferred. The calculations were based on the double-harmonic-oscillator approximation which relates the intensity to the square of the derivative $d\mu^{ind}/dQ$, where μ^{ind} is the field-induced dipole moment and Q is a normal coordinate. Since only inductive effects were considered, the treatment parallels that for the vibrational-Stark-effect intensity (Bishop 1993). For N_2 $d\mu^{ind}/dQ$ is related to $d\alpha/dQ$ and for CH_4 to $d\mu/dQ$ and $d\alpha/dQ$. Because the signs of the components of $d\alpha/dQ$ were not known for N_2, it was not possible to give a definitive value for the effective field. For CH_4, the intensity of the ν_3 line was not compatible with the experimental results. Certain improvements were suggested, e.g. including hyperpolarizabilities (β) in the induced dipole moment (what will be required, in fact, are the derivatives of β with respect to Q, and these are hard to come by) and introducing a field gradient term.

As with the frequency shifts, so for the intensity shifts: it would be nice to have *ab initio* calculations of the trapped species interacting with the cation, as well, perhaps, with the other neighbouring ions. Configuration optimization could be performed and, through the pair properties, the frequency and intensity shifts found. Comparison of the results (which would include all electrostatic, inductive, dispersive, and repulsive contributions) with experiment would then determine just how much of the zeolite cage affects the infrared spectrum of the trapped species. In this context, it should be mentioned that Grodzicki *et al.* (1988) have performed approximate calculations (self-consistent-charge Xα model) for Ca–OCO, Ca–ONN and Ca–NNO in order to estimate vibrational frequency changes for CO_2 and N_2O in Ca*A*.

Though not strictly a part of this review, a study on the infrared shifts of HF (and certain hydrogen-bonded complexes) in different rare gas matrices should be mentioned (Hannachi and Ángyán 1991).The reason is that these authors model the perturbing environment by a self-consistent reaction field (see § 2.1), i.e. the model used in solvent-shift theories, and this approach fits with the philosophy of the present article. Hannachi and Ángyán find that dispersive and repulsive interactions will be necessary to bring the theory into concordance with the experimental results.

3.2. *Nonlinear optics*

In the scheme of this review, this is the one piece of the jig-saw puzzle which is missing: nonlinear optical investigations for species trapped in zeolites. As far as the author knows there have been neither experimental nor theoretical studies of this subject. Though technical problems may beset such experiments, they would be as interesting as any that might be carried out for fullerenes. Information thus gained would make a useful bridge between nonlinear optical measurements in the gas phase and those carried out in the liquid phase.

3.3. *Nuclear magnetic shielding*

This section is mainly concerned with the investigations that have been undertaken by C. J. Jameson and co-workers on noble gases in zeolites. In 1992 Jameson *et al.* reported nuclear magnetic resonance (NMR) spectroscopic studies of xenon clusters trapped in Na*A*. The equilibrium distributions in the α cages did not conform with the previously proposed statistical models and they concluded that the reason for this was the importance of the attractive Xe–Xe interactions. This led them to make *ab initio* calculations of the intermolecular shielding in Ar–Ar and Ar–Na^+ (Xe–Xe being beyond their computational resources); calculations which were later reported in more detail by Jameson and de Dios (1992). The experimentalist's choice of Xe, which would not be the theoretician's, is based on the large chemical shifts and sensitivity to intermolecular interactions associated with this species. Two conclusions in the original paper are of interest: (*a*) that there is no single special site near the unique Na_{III} ion in the cage which is favoured for xenon (compare this with the deductions of Cohen de Lara *et al.* 1990), (*b*) the interactions of the Xe atom with the cations of the cage are not nearly as large as the chemical shifts due to Xe–Xe interactions. The last point leads to the observation that, from the theoretical standpoint, experiments at low loading, where only a single atom occupies the cage, will be of most interest when it comes to studying the interactions between trapped and trapper.

In the second paper, Jameson and de Dios (1992) gave the results of the first *ab initio* calculation of an intermolecular chemical shielding function for a pair of interacting atoms. Though this research stemmed from the earlier xenon-clusters-in-zeolites work, it obviously has a role to play in the theory of NMR for noble gases in the liquid phase (just the sort of cross-over which is the raison d'être for this review). Calculations were performed for Ar... Ar, Ne... Ne, and Ar... Na^+ and a scaling procedure was used to obtain the intermolecular shifts related to xenon.

The framework of the calculations was the localized orbital localized origin (LORG) approach of Hansen and Bouman (1985). A technique which ensures that the value of the magnetic shielding is approximately gauge invariant. This is, essentially, a random-phase-approximation (RPA) technique and does not account for second-order electron correlation. Since consideration of the latter is necessary for a good account to be given of the long-range van der Waals dispersive interactions, calculations were also carried out using second-order LORG (SOLO).

Comparison of the intermolecular shielding functions was made by looking at the second virial coefficient of the NMR chemical shift in the gas phase. The required formulas were:

$$\sigma(T,\rho)=\sigma_0(T)+\sigma_1(T)\rho+\sigma_2(T)\rho^2+\dots, \tag{37}$$

where ρ is the density, and

$$\sigma_1(T)=\int_0^\infty 4\pi R^2\,dR[\sigma(R)-\sigma(\infty)]\exp[-V(R)/kT]. \tag{38}$$

Here, R is the interatomic separation and $V(R)$ the potential function. Agreement between the measured and calculated second virial coefficients, $\sigma_1(T)$, gave credence to the *ab initio* interatomic shielding functions. It may be noted that equation (38) is fundamentally the same as equation (24).

The difference between the LORG and SOLO calculations for Ar–Ar was small, suggesting that second-order electron correlation contributions are surprisingly unimportant for this system. However, much greater changes were found for Ar–Na^+, suggesting that electron correlation is more important for induction than dispersion, contrary to conventional wisdom. Of further importance, in comparing these two interactions, is the fact that a neighbouring cation had a much smaller contribution to the Ar shielding than an Ar atom at the same distance.

The authors also considered the $-74{\cdot}8$ ppm experimentally-determined chemical shift between a single Xe atom in a Na*A* α cage and the isolated atom. To interpret this they used the Drude model of two interacting atoms and the Schmeits–Lucas (1976, 1983) model of the zeolite cage idealized as a spherical cavity in a solid continuum. The approximate formula for the shift was given as:

$$\sigma(R)-\sigma(\infty)\cong -(BU/a^3)[1-(R/a)^2]^{-3}/(4\pi\epsilon_0), \tag{39}$$

where R is the distance from the centre of the cavity of radius a, U is the first ionization energy and B is the mean shielding polarizability, see equation (26). Reasonable values of R, a, and U and an old estimate of B ($9{\cdot}8\times 10^4$ ppm a.u.$^{-2}$) gave a shift of approximately -66 ppm. However, a more recent SCF estimate of B for Xe (Bishop and Cybulski, 1993b, 1994) is considerably smaller ($4{\cdot}4\times 10^3$ ppm a.u^{-2}) and, when this value is used, the fair agreement with experiment for the shift is lost, suggesting that the model employed is much too crude. A corollary to this model (not made by the authors), would assume the experimental shielding shift to be entirely dispersive in nature (i.e. $-B\overline{F^2}$) and this leads, with the recent value of B, to an effective field of $\sim 0{\cdot}13$ a.u. This is much larger than any previous estimates (Cohen de Lara *et al.* 1992) and it is undoubtedly incorrect. Again, a simple treatment of the atom–cage interaction does not appear to work.

In their latest work Jameson and de Dios (1993) have carried out LORG calculations for the magnetic shielding of ^{23}Na in NaH, ^{39}Ar in ArNe, ^{21}Ne in NeH and ^{39}Ar in Ar…NaH for a wide range of intermolecular separations. From their results, they suggest a possible universal shape for the shielding function for any two-atom system. As well, they determine that the R dependence of the *ab initio* shielding functions in the *long-range* limit for a noble gas atom in the presence of a neighbour is consistent with the mean field model. It would be profitable to tie some of these ideas and results to the gas–liquid shifts which have been measured for the noble gases (Seydoux *et al.* 1993).

As a word of warning on the interpretation of chemical shifts in zeolites, attention is drawn to the paper by Ito and Fraissard (1982). They measured the pressure dependence of the shifts for Xe absorbed in a number of different zeolites. They concluded that the shifts in the cases of NaY_2, HY, and *GA* were entirely due to Xe-cage wall and Xe–Xe *collisions*. Whatever the truth of this assertion, it is wise to remember that, both for NMR and vibrational spectroscopy on trapped species, the object of interest does not necessarily stand still.

Finally, the Xe shift due to the walls of the zeolite, rather than the counterion (e.g., Na^+) has been deduced experimentally by Boddenberg and Hartmann (1993). They ran xenon NMR experiments on a series of zeolites in which more and more Cu^{2+} (outside the cage) replaced the Na^+ ions. From a plot of the shift against the Na^+ concentration, they found the intercept to be 32 ppm. They, therefore, assigned this value to interactions of xenon with the cage framework.

4. Conclusions

The intent of this review has been to draw together investigations of physical phenomena which, at first sight, would seem to be disparate. The conjunction will hopefully stimulate progress in all these areas through the cross-over of ideas. There is no question, however, that, as opposed to gases, the theoretical treatment of the liquid and solid phase is a much more difficult task.

It is clear that a lot of work has been done, but many questions remain unanswered. Here are a few. What is the correct way of determining the shape and size of a cavity in a solution? How can the self-consistent reaction field (SCRF) model be adapted for non-polar solutes? Can it? Can such a model be used for NMR gas to liquid shifts? If so, how? Can a simple model for zeolites be constructed which would simultaneously account for the infrared spectrum and the magnetic shielding of an embedded species? Can the SCRF model be used for nonlinear optical experiments in the liquid phase? Or, is there a perturbation-theoretic alternative which is better? Could direct *ab initio* methods be used for the first solvent layer in a solution and only approximate ones for the rest of the solvent? What about discontinuities?

Some things which can be done and which would help are the following: more *ab initio* calculations of the effects of electric fields (uniform and non-uniform) on basic molecular properties such as vibrational frequencies, magnetic shieldings, polarizabilities; *ab initio* calculations of energies, frequencies, polarizabilities, and shielding constants for molecules perturbed by an alkali or alkaline earth atom; similar calculations using perturbation theory.

Acknowledgments

The author thanks Drs E. Cohen de Lara and W. T. Raynes for their helpful comments and the Natural Sciences and Engineering Research Council of Canada for financial support.

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