CHAPTER 1

Fundamental Intramolecular and Intermolecular Information from NMR in the Gas Phase

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1.1 Why Should One Do Gas Phase NMR Measurements?

In the gas phase we have a well-defined homogeneous physical system, and the theory for dilute gas behavior is in an advanced stage. In dilute gases, we can expand the molecular electronic property (*e.g.*, nuclear magnetic shielding, J coupling, nuclear quadrupole coupling) in a virial expansion, in which the property virial coefficients can be expressed theoretically in closed form and can be obtained unequivocally experimentally in the binary interaction limit. These experimentally measured quantities depend on two quantum-mechanical mathematical surfaces: the shielding, or J, or electric field gradient (efg) at the nucleus as a function of intermolecular nuclear coordinates and the weak intermolecular interaction potential energy surfaces that are also a function of the same intermolecular nuclear coordinates. Furthermore, we can extrapolate the measured NMR data (shielding, J, efg) to the zero-density limit to obtain these electronic properties for the

isolated molecule, that are much more closely related to quantum-mechanical calculations than quantities measured in condensed phases. To validate theoretical methods, it is always preferable to benchmark the results by comparing them with available experimental data, preferably for isolated molecules. Extrapolation to this limit is only possible for gas phase measurements. Here too, the temperature dependence of the electronic property at the zero-density limit is a function of two quantum-mechanical mathematical surfaces: the shielding (or J or efg) as a function of intramolecular nuclear coordinates and the intramolecular potential energy surface that are also a function of the same coordinates. The latter is commonly characterized by specifying the derivatives at the equilibrium intramolecular configuration, namely the quadratic, cubic, quartic force constants. The shielding is particularly sensitive to the anharmonicity of the intramolecular potential surface. Thus, gas phase NMR data for shielding, J, and efg provide stringent tests of theoretical descriptions of both the quantum-mechanical electronic property surfaces and also the potential energy surfaces over which they are averaged, to yield the temperature-dependent experimental data (property virial coefficients and zero-density limiting values) that are available only in the dilute gas phase. In addition to temperature, another variable, isotopic masses of neighboring (and observed) nuclei, can affect the measured data, given the same electronic property surfaces and the same potential energy surfaces; thus, isotope effects provide an independent test of these quantum-mechanical surfaces. While these observations and their interpretation are of specific interest to NMR spectroscopists, they are of more general interest as prototypes of rovibrational averaging and intermolecular effects on molecular electronic properties. Fortunately, it is possible in NMR spectroscopy to make very precise measurements of quantities that are very sensitive to changes in electronic environment, nuclear magnetic shielding and J, molecular electronic properties that are sensitive indices of the chemical bond and that vary with nuclear displacements from the equilibrium molecular configuration, leading to changes in resonance frequencies that are amenable to highly precise measurements under precisely controlled constant temperature conditions over a wide range of temperatures. Thus, gas phase measurements in NMR provide valuable tests of quantum-mechanically calculated molecular electronic property surfaces. Indeed, the dihedral-angle dependence of three-bond J coupling by Martin Karplus (known to NMR spectroscopists as the Karplus equation) was the earliest (1959) example of an experimentally testable quantum-mechanically calculated property surface.[1] An important disadvantage of gas phase NMR, however, is that only the isotropic values of the NMR tensor quantities can be obtained.

For the same reasons, NMR spectra of dilute gases provide thermodynamic and kinetic information that are important from a theoretical point of view. The gas phase allows the separation of intramolecular and environmental effects on the energy requirements for molecular processes. Gas phase NMR data provide the free energy barriers for conformational

changes, from which torsional parameters for molecular dynamics (MD) force fields are obtained. Furthermore, pressure can be used as an experimental variable in gas phase studies; rate constants are both temperature- and pressure-dependent. Use of dynamic gas phase NMR techniques permits the complete characterization of rate processes within both temperature and pressure ranges, allowing the kinetics of chemical rate processes to be investigated in both the unimolecular and bimolecular regimes. Information about internal vibrational redistribution and collisional energy transfer in kinetic processes is obtained from these NMR studies. Thus, conformational dynamics can be characterized under well-defined limiting conditions in the gas phase, free energy barriers can be obtained, and theoretical interpretation of results using well-established methods can provide detailed interpretation. A collateral experimental advantage is the rapid spin–lattice relaxation that facilitates multiple acquisitions; ^{13}C relaxation times are at least two orders of magnitude shorter in the gas phase for some systems than in condensed phases. In the gas phase, we can measure spin–lattice relaxation rates that are of fundamental interest in their own right. The rates are resolvable into well-defined mechanisms *via* measurements as a function of field, of temperature, of density. Furthermore, in the gas phase, each relaxation mechanism is capable of being theoretically calculated *via* classical trajectory calculations in the binary collision limit, yielding well-defined relaxation cross-sections that are well-established descriptions of fundamental dynamic molecular events, such as transfer of rotational angular momentum and molecular reorientation, that provide valuable stringent tests of the anharmonicity of intermolecular potential surfaces.

Reviews of gas phase NMR studies include some of these measurements of shielding and spin–spin coupling,[2–5] spin-relaxation studies,[3] and conformational changes,[4,6,7] that provide more detailed information and references to original literature not included in the present overview.

1.2 The Effect of Intermolecular Interactions on NMR Chemical Shifts

Buckingham and Pople proposed in 1956 that any electromagnetic properties of gases be expanded in a virial expansion.[8] For nuclear magnetic shielding in a pure gas

$$\sigma(T, \rho) = \sigma_0(T) + \sigma_1(T)\rho + \sigma_2(T)\rho^2 + \sigma_3(T)\rho^3 + \cdots \tag{1.1}$$

For a nucleus X in molecule A in a dilute mixture of gases A and B,

$$\sigma^{X\,in\,A}(T, \rho_A, \rho_B) = \sigma_0^{X\,in\,A}(T) + \sigma_{1AA}(T)\rho_A + \sigma_{1AB}(T)\rho_B + \cdots \tag{1.2}$$

In the gas of pure A, this expansion permits the study of the intermolecular contributions by investigating the temperature dependence of the density coefficient of nuclear shielding $\sigma_{1AA}(T)$, *i.e.*, the slope of $\sigma^{X\,in\,A}(T, \rho_A)$ as a function of density ρ_A, in the limit of linear behavior. At the same time this

permits the study of the intramolecular contributions, $\sigma_0^{\text{X in A}}(T)$, by investigating the temperature dependence of nuclear shielding in the limit of zero gas density. This term arises from the variation with temperature of the populations of the rotational and vibrational states, each one of which has a different characteristic average shielding. This is mathematically equivalent to extrapolation to a pressure that is low enough that collisional deformation of the molecules no longer contributes to σ, however there are still sufficient collisions to provide averaging over the rovibrational states of the molecule. The quantity $\sigma_0^{\text{X in A}}(T)$ is the shielding in a molecule free of intermolecular interactions and therefore equivalent to an isolated molecule. From experimental measurements in the linear-density regime, each observed shift can be corrected for the intermolecular contributions $\sigma_1(T)\rho$ so that the remainder, $[\sigma_0(T) - \sigma_0(300\ \text{K})]$, is obtained.

In gas mixtures with low mole fraction of A in B, subtraction of the accurately determined AA contributions permits the determination of $\sigma_{1AB}(T)$. The quantity $\sigma_{1AA}(T)$ is a measure of the effects on nuclear magnetic shielding of X in molecule A from binary collisions of A with another A molecule and $\sigma_{1AB}(T)$ is a measure of the effects from binary collisions of A with molecule B. The excess intermolecular property, $\sigma_2(T)\rho^2 + \sigma_3(T)\rho^3 + \cdots$, has been investigated in some cases, for example for ^{129}Xe in Xe gas, where collectively this has been found to be opposite in sign to $\sigma_1(T)\rho$.[9] There are experimental indications that this is true for other nuclei in other gases as well, for example, ^{19}F in $H_2C{=}CF_2$.[10] Our main focus in this section is on the density coefficient of NMR properties in the limit of zero density, that is, the second virial coefficient of shielding. There is an experimental quantity that also has a linear density dependence, the bulk susceptibility contribution to the observed chemical shift,[11] that is the same amount for all nuclei in the sample, that is an artifact of the sample shape and vanishes for spherical samples. It is understood in this section that experimental values of the second virial coefficient will have been corrected for the sample shape contribution, since we are interested in the true shielding response that arises from binary intermolecular interactions. This susceptibility correction limits the precision of experimental values, but is of consequence only in those cases where the true second virial coefficient of shielding is smaller than this correction.

1.2.1 The Density Coefficient of the Chemical Shift

The first observation of the density coefficient of the chemical shift in a gas was by Streever and Carr in 1961 for ^{129}Xe in xenon gas,[12] followed soon thereafter by Gordon and Dailey for ^{1}H in CH_4 and C_2H_6,[13] and in 1962 by Raynes, Buckingham, and Bernstein for ^{1}H in H_2S, CH_4, and C_2H_6 and for HCl in various gas mixtures.[14] Measurements of the second virial coefficient of nuclear magnetic shielding have been carried out for a variety of nuclei; the largest values are those for ^{129}Xe in Xe atom interacting with another rare gas atom or molecule.[9,15-19] Second virial coefficients of shielding of other

nuclei, for example, of ^{1}H in HCl, HBr,[20] HCN,[21] NH$_3$,[22] C$_2$H$_4$, C$_2$H$_6$, C$_3$H$_8$,[23] of ^{11}B in BF$_3$,[24] of ^{13}C in CO,[20] CO$_2$,[25] HCN,[21] CH$_4$,[23,24] of ^{15}N in N$_2$,[26] NNO,[25] NH$_3$,[22] of ^{17}O in CO, CO$_2$, NNO, OCS,[27] of ^{31}P in PH$_3$,[28] PF$_3$, PF$_5$, POF$_3$,[29] of ^{19}F in a large number of molecules (ref. 30, 31 and references therein) have been investigated as a function of temperature. Recent additions to these include all the nuclei in propene,[32] in cyclopropane,[33] in CHF$_3$,[34] in CH$_2$F$_2$,[35] in SO$_2$ and SO$_3$,[36] in SiF$_4$,[37] in CH$_3$OH,[38] in (CH$_3$)$_2$O,[39] in CH$_3$NH$_2$,[40] in CH$_3$CN,[41,42] and in (CH$_3$)$_4$Sn.[43] The linear-density coefficient of ^{13}C in benzene, acetylene, and CH$_3$Br,[44–46] and of ^{33}S in SF$_6$[47] have also been studied.

An advantage of gas phase studies in the linear-density regime is that the intermolecular effects on shielding can be expressed in closed mathematical form, just as derived in general for any electromagnetic molecular property by Buckingham and Pople.[8] For Xe interacting with CF$_4$, for example,

$$\sigma_1(T) = \iiint \{\sigma(R,\theta,\phi) - \sigma(\infty)\} e^{\left[\frac{-V(R,\theta,\phi)}{k_B T}\right]} R^2 \, dR \sin\theta \, d\theta \, d\phi \qquad (1.3)$$

The theoretically expected behavior of $\sigma_1(T)$ in rare gas systems over a wide temperature range has been shown to be negative (deshielding with in-creasing density), increasing in magnitude with increasing temperature, then switching over and decreasing in magnitude with increasing tem-perature (see Figure 6 in Ref. 48). For rare gas atoms, it has been found that the sign of $\sigma_1(T)$ is indeed negative at all temperatures, that is, the nucleus becomes more deshielded with increasing density. For nuclei of end atoms in a molecule, the sign of σ_1 is generally negative at all temperatures. Known exceptions are $\sigma_1(^{15}$N) in CH$_3$CN and HCN,[21,41] in which intermolecular interactions involve the lone pair and thereby affect $n \rightarrow \pi^*$ contributions to the ^{15}N shielding toward less deshielding (such as that which accompanies a blue shift in the $n \rightarrow \pi^*$ transition energy). For more centrally located nuclei in a molecule, the general behavior, sign, or temperature dependence has not been calculated, but magnitudes are expected to be smaller than for end atoms. This behavior is not generalizable since, unlike the end atoms which experience intermolecular effects directly, a nucleus in centrally located atoms (except in linear molecules) can only experience intermolecular effects indirectly through chemical bonds, hence is dependent on the specific molecular structure surrounding the observed nucleus. In those cases where the temperature dependence has been measured over a wide range of tem-peratures, it has been found that the magnitude of $\sigma_1(T)$ generally decreases with increasing temperature; exceptions are ^{129}Xe in CO and ^{129}Xe in N$_2$,[19] which are not anomalous behavior since $\sigma_1(T)$ has been theoretically pre-dicted to turn around to decreasing magnitudes at much lower tempera-tures, in general.[48] The magnitudes and signs of very small σ_1 for less exposed nuclei such as ^{33}S in SF$_6$, ^{13}C in CH$_4$, ^{29}Si in SiF$_4$[37,47,49] are difficult to obtain accurately in experiments because they are generally small and the experimental density coefficient is thus dominated by bulk susceptibility contributions for non-spherical sample shapes.

There is clear evidence of a nuclear site effect in the same molecule, with more exposed nuclei having larger values of σ_1 than less exposed ones.[50] In a clear example, the three chemically inequivalent F nuclei in $XFC=CF_2$, F_{gem}, F_{trans}, F_{cis}, have different distances from the center of mass of the molecule, and these relative distances change as X goes from light to heavy mass. Within the freely rotating molecule, the relative exposure of each of the three ^{19}F sites to intermolecular interactions are reflected in their respective values of σ_1 in $XFC=CF_2$ molecules (X = H, F, Cl, Br, I), completely consistent with the relative distance of each of F_{gem}, F_{trans}, F_{cis} from the center of mass as the latter changes systematically from X = H, to F, to Cl, to Br, to I. A more transparent and elegant example of the nuclear site effect was demonstrated experimentally by Beckett and Carr in the density dependence (in HD gas of varying density with a small amount of D_2) of the isotope shift $[\sigma(D_2) - \sigma(HD)] = a + b\rho$.[51] Here, $a = [\sigma_0(D_2) - \sigma_0(HD)]$ is the isotope shift extrapolated to the zero-density limit. Their observation that the density coefficient of the isotope effect, $b < 0$ means that $|\sigma_1(D_2)| > |\sigma_1(HD)|$ since all σ_1 is known to be negative. The greater magnitude of $|\sigma_1(D_2)|$ arises from the more exposed deuterium nucleus in D_2 ($R/2$ from the center of mass in this isotopomer) compared to HD where the D is $R/3$ from the center of mass. The density coefficient b can be calculated from the site factors, as shown in ref. 50. Thus, the nuclear site effect gives rise to the observed density dependence of the isotope shift in the Beckett and Carr experiments.

In some cases, intermolecular effects on shielding have been measured from very low density gas to the liquid phase in a single experiment. It is especially interesting when both gas and liquid are observed in the same sample tube as a function of temperature. The difference in chemical shift between the liquid and the overhead vapor should approach zero in the limit of the critical temperature. Indeed, this behavior has been observed for ^{19}F in a large number of compounds (see for example ref. 50).

1.2.2   The Intermolecular Shielding Function

The first *ab initio* shielding function calculated for a rare gas pair $[\sigma(R) - \sigma(\infty)]$ was that for Ar–Ar;[48] these were restricted Hartree–Fock (RHF) calculations of $\sigma(R)$ from large separations all the way to an internuclear distance of 1 Å, or 0.30 times r_0(Ar–Ar). In this specific case the united atom in the correlation diagram of the two Ar atoms is a closed shell ground state (Kr) so that it is possible to extrapolate the shielding function all the way to the united atom, and thereby observe the general shape of an intermolecular shielding function. The intermolecular shielding function for Xe interacting with rare gas atoms Ne, Ar, Kr, Xe has been calculated with very large basis sets at various levels of accuracy.[52,53] With the inclusion of relativistic corrections,[53] the final agreement with the experimental temperature dependence is almost within experimental error. The shielding functions all change steeply in the vicinity of r_0 of the potential energy surface (PES).

It turns out that scaling is possible for rare gas pairs using the shielding sensitivity that is proportional to $\langle a_0^3/r^3 \rangle$ for the atom whose shielding is being calculated and using the corresponding-states type of factors for the strength of intermolecular interactions, in terms of electric dipole polarizabilities α and ionization potentials IP:[54]

$$\frac{\alpha_{Xe}(0)}{\alpha_{Rg}(0)} \frac{IP_{Xe}}{IP_{Rg}} \frac{IP_{Xe} + IP_{Rg}}{2IP_{Xe}}$$

This has been shown both at the RHF and DFT (Density Functional Theory) level by comparing *ab initio* calculated shielding functions for various rare gas pairs with scaled shielding functions based on the Ar–Ar pair.[52]

What is the range of interaction measured by the intermolecular chemical shift, *i.e.*, which distances make the major contributions to the observed density coefficient of the chemical shift? We answered this question using ^{129}Xe shielding in rare gas pairs.[52] This is clearly shown by the reduced function that compares all three rare gas pairs at their corresponding states. When the integrands in $\sigma_1(T) = 4\pi \int_0^\infty \{\sigma(r) - \sigma(\infty)\} \exp[-V(r)/k_B T] r^2 \, dr$ for Xe-Rg, Rg = Xe, Kr, Ar, Ne are scaled using the scaling factor $\{[\alpha_{Xe}(0)/\alpha_{Rg}(0)] \cdot [IP_{Xe}/IP_{Rg}] \cdot [(IP_{Xe} + IP_{Rg})/2IP_{Xe}]\}$ and $r^* = r/r_0$ then at the reduced temperature $T/T_c = 1$ all the integrand functions superimpose into one curve when plotted *vs.* r^*. From this curve we find that $\sigma_1(T)$ is nearly entirely accounted for by the sum over the range $0.90r_0$ to $1.5r_0$, with $r = 0.96r_0$ to $1.24r_0$ providing approximately 80% of the observed density dependence of the nuclear shielding for rare gas pairs.[52] This is the range of interaction measured by the intermolecular chemical shift when only van der Waals (vdW) interactions are involved. *Ab initio* calculations of Xe shielding for Xe atom interacting with small molecules such as N_2, CO_2, CO, CH_4 and CF_4[55,56] and in cages such as C_{60} and $(H_2O)_n$[57] indicate that the sharp deshielding that is observed in the Xe-Rg shielding function for interatomic distances shorter than the r_0 of the potential function is also observed in these later examples. State-of-the-art coupled-cluster calculations of the intermolecular shielding surface for hetero and homo rare gas pairs among the set Ar, Ne, and He[58] exhibit the same general behavior of $[\sigma(R) - \sigma(\infty)]$ and of $\sigma_1(T)$ for all rare gas pairs, as was already described above, found earlier with RHF calculations for these systems.[48]

The observed scaling discussed above permits us to predict that $\sigma_1(T)$ for ^{1}H will be small so that the density coefficient will be dominated by the sample-shape-defined bulk susceptibility contribution, and $\sigma_1(T)$ for other nuclei in end atoms in molecules will scale with $\langle a_0^3/r^3 \rangle$ for the atom, just as the chemical shift ranges for different nuclei do.[59] Of course, when the observed nucleus is in a molecule with structure, any secondary effects such as changes in torsion angles resulting from the intermolecular interactions may contribute significantly to the intermolecular shifts observed for the nucleus in question. Also, where hydrogen bonding is involved, the

shielding of the donor atom, the acceptor atom and the proton should be affected significantly, though not in the same monotonic way as for rare gas pairs. To our knowledge, there has been no equivalent investigation to determine the range of interaction measured by the intermolecular chemical shift in a hydrogen-bonded system.

1.2.3   Contact Shifts in the Gas Phase

For interactions with a paramagnetic gas, in addition to the $\sigma_1(T)$ that would be present for the diamagnetic gas, there is a contribution coming from the electron spin density at the position of the observed nucleus. For example, for Xe interacting with O_2,

$$\sigma_1(T)_{\text{hyperfine}} = -\left(\frac{16\pi g_e^2 \mu_B^2}{9k_B T}\right) 2\pi \iint \left[\rho_{\text{spin}}(R, \theta) - \rho_{\text{spin}}(\infty)\right] e^{\left[\frac{-V(R,\theta)}{k_B T}\right]} R^2 dR \sin \theta \, d\theta$$

(1.4)

and, of course, the molar paramagnetic bulk susceptibility of the paramagnetic gas provides a large but predictable sample-shape-specific contribution. In eqn (1.4), the sign of the electron spin density at the Xe nucleus, $[\rho_{\text{spin}}(R,\theta) - \rho_{\text{spin}}(\infty)]$, is negative when the probability density of the β spin dominates over the α at the Xe nuclear position (R,θ). The linear-density coefficient for Xe in O_2 and NO have been obtained as a function of temperature.[60–62] The calculation of the ^{129}Xe hyperfine tensor of the Xe@O_2 molecular system permits comparison with the experimental data.[63] At low temperatures, the explicit T^{-1} dependence in the hyperfine contribution dominates over the weaker temperature dependence in the intermolecular weighting factor. Thus, a sample of Xe in O_2 can serve as a very sensitive thermometer in NMR measurements.

1.3   The Intramolecular Effects on Shielding

Experimental intramolecular effects on shielding have been reviewed earlier,[2,64,65] and also as a subset of the more general concept of rovibrational averaging of molecular electronic properties.[66] These manifest themselves as isotope shifts and temperature dependence in the isolated molecule. In 1952 Norman Ramsey considered the vibrational and rotational averages of shielding and spin–spin coupling for the case of diatomic molecules, using hydrogen molecule and its isotopomers as specific examples.[67] Although temperature-dependent shieldings due to rovibrational averaging in isolated molecules were already predicted by Buckingham in 1962,[68] our first observations of the temperature dependence of shielding in isolated molecules occurred in 1977 in the determination of $\sigma_1(T)$ for ^{19}F in the small molecules F_2 and ClF,[20] followed by ^{19}F in BF_3, CF_4, SiF_4, and SF_6.[69] We explored ^{19}F rather than ^{1}H chemical shifts in studying molecules in the gas phase because of the known large chemical shift range for ^{19}F nucleus, in addition

to its being an end atom more exposed to intermolecular interactions. Extrapolation of our measured ^{19}F chemical shifts to zero density revealed intercepts that were strongly temperature-dependent, thus leading to our investigation of the temperature dependence in the limit of the isolated molecule, not only for ^{19}F in a large number of molecules, but also for other nuclei such as ^{31}P, ^{15}N, and others. We explored the concept of the shielding surface for a nucleus in a molecule, the dependence of the nuclear magnetic shielding on bond distances, bond angles, and other internal degrees of freedom in a polyatomic molecule, by starting from the observed temperature dependence and extracting information about derivatives of the intramolecular shielding surface. Raynes, on the other hand, from 1971 on, started from the theoretical shielding surface and tried to predict the magnitudes of the temperature dependence and the mass dependence, so he was inclined to start with ^{1}H in H_2,[70,71] and H_2O,[72,73] and ^{1}H and ^{13}C in CH_4,[74-76] since the accuracy of quantum calculations of shielding were limited by the number of electrons in the molecule and the size of the set of basis functions. On the other hand, for ^{1}H, the temperature dependence of shielding in the isolated molecule is small and, thus, difficult to accurately measure experimentally. H_2O is particularly difficult to observe as an isolated molecule.

1.3.1 The Temperature Dependence of Chemical Shift in the Zero-density Limit

We measured the temperature dependence of the shieldings for ^{13}C in CO and CO_2,[26,25] [15]N in N_2 and NNO,[26,25] [31]P in PH_3,[28] [11]B in BF_3 and ^{13}C in CH_4,[24] [31]P in PF_3 and POF_3,[29] [15]N and ^{1}H in NH_3,[22] and ^{19}F in a large number of fluorine-containing molecules (references for individual ^{19}F sites are given in ref. 30 and 31). For most cases, the temperature dependence of shielding in the isolated molecule is non-linear and has a negative $d\sigma_0/dT$ throughout the temperature range, that is, more deshielding with increasing temperature. The largest temperature dependence we observed was for ^{19}F in F_2 molecule.[20] Here, as well as in all other [19]F $\sigma_0(T)$ that we reported for a large number of fluorohydrocarbons, the slopes $d\sigma_0/dT$ are negative and the curvature is in a uniform direction, more pronouncedly negative with increasing temperature. This we also observed for ^{19}F in SF_6, SeF_6, TeF_6, and WF_6.[77] There is an interesting correlation between the absolute shielding in the isolated molecule σ_0 and the temperature coefficient $d\sigma_0/dT$ for ^{19}F; the more deshielded ^{19}F sites also have the largest temperature coefficients.[78,79] The R_e that minimizes the molecular potential energy at the equilibrium geometry of a diatomic molecule, for example, is correlated with the quantum-mechanical behavior of the electrons which determines the steepness of the shielding function at that position, as will be seen in Section 1.3.2. The curvature of the $\sigma_0(T)$ function is an expected natural consequence of the non-linear dependence on temperature of the dynamically averaged displacements of the bond length from its equilibrium value. Notable exceptions are $\sigma_0(T)$ functions for ^{13}C in CO and ^{15}N in N_2,[26] which appear to

be linear. When centrifugal distortion dominates the dynamically averaged displacement of the bond length from its equilibrium value, $(\langle R \rangle^T - R_e)$, and when the shielding surface is nearly linear at the equilibrium geometry for the molecule, then a linear $\sigma_0(T)$ may be expected over a wide temperature range. Raynes *et al.* reported linear temperature dependences for the ^{1}H and ^{13}C in CH_4, C_2H_6, C_2H_4, C_3H_8 and other alkanes, with predominantly negative values of $d\sigma_0/dT$ for ^{1}H, and either sign for ^{13}C.[23] The predominantly negative values of $d\sigma_0/dT$ observed for nuclei of end atoms could be rationalized in terms of dominant local bond anharmonic stretching that leads to average bond lengths that increase with increasing temperature and implies $(\partial\sigma/\partial r)_e < 0$ for those systems. We shall see in Section 1.3.2 that this is not always the case. Negative values for $d\sigma_0/dT$ have also been observed for central atoms, such as ^{13}C in CH_4,[23,24] ^{77}Se in SeF_6 and ^{126}Te in TeF_6,[77] where the totally symmetric breathing mode is largely responsible for the observed $d\sigma_0/dT$. On the other hand, the ^{13}C nuclear sites in ethane and higher alkanes are involved in many vibrational modes of the appropriate symmetry, so the sign of $d\sigma_0/dT$ is less easily predicted.

1.3.2   The Intramolecular Shielding Surface for Diatomic and Polyatomic Molecules

The first complete intramolecular shielding surface was calculated in 1979 by Hegstrom for the entire range ($R = 0$ to ∞) for $\sigma_\perp$ and $\sigma_{||}$ for H_2^+ molecule ion:[80] At $R = 0$ the shielding is characteristic of the diamagnetic shielding of He nucleus in free He^+ ion (the united atom for this system) and at $R = \infty$ the smaller diamagnetic shielding of an isolated H atom, passing through a minimum at R longer than R_e, so that at $R = R_e$, the derivative of the shielding function is negative. Earlier, some calculations of nuclear shielding in the immediate vicinity of the equilibrium bond length had been reported for a few diatomic molecules, *e.g.*, ^{1}H and Li in LiH by Stevens and Lipscomb (1964),[81] in H_2 by Raynes *et al.* (1971),[70] so that the first and second derivatives of the shielding with respect to bond length could be determined at the equilibrium geometry of the molecule. Later, Chesnut calculated first derivatives of the isotropic shielding at the equilibrium geometry for a number of nuclei in small molecules (including all hydrides across the periodic table from LiH to FH and NaH to ClH) and found that all derivatives for ^{1}H shielding in these molecules were negative, that is, at the equilibrium geometry, the ^{1}H shielding surface is becoming deshielded with slight increase in bond length. On the other hand, while most shielding derivatives were negative for the heavier nucleus in the hydride molecules, some were positive.[82] We obtained the same shape of the shielding surface for ^{23}Na in NaH between 0.5 and 5.0 Å[54] as Hegstrom obtained for H_2^+ molecule ion, except that the ^{23}Na shielding surface has a minimum at R shorter than R_e, so that at $R = R_e$, the first derivative of the shielding function is positive (likewise for Li in LiH), just as found by Chesnut. On the other hand, for ^{19}F in F_2 and ^{35}Cl in ClF and for ^{19}F in HF and ^{35}Cl in HCl, the

shielding functions are decreasing with distance in the vicinity of R_e, that is, $[d\sigma/d(R - R_e)]_e < 0$. The general behavior of $[d\sigma^X/d(R - R_e)]_e$ across the periodic table for XH_n hydrides going from LiH to FH and going from NaH to ClH is to smoothly vary with R_e from positive to negative across a row. Furthermore, as a description of the general behavior across the periodic table, we found that all 14 cases could be placed on one curve, if $[d\sigma^X/d(R - R_e)]_e$ were scaled by $\langle a_0{}^3/r^3 \rangle_X$ and R_e.[54]

The highest level of theory is to have a full treatment of electron correlation, *i.e.*, full configuration interaction (FCI) calculations in the basis set limit. This is rarely used except for the smallest systems. To include electron correlation at all, we go beyond self-consistent field (SCF), *i.e.*, Hartree–Fock calculations. The most accurate of the single reference methods, yet still practically feasible, treats electron correlation at a level of coupled clusters singles, doubles and a perturbation correction for triple excitations, CCSD(T). When a single reference calculation is insufficient, multi-configurational methods are used, for example MCSCF (multi-configuration self-consistent field), RASSCF (restricted active space SCF), CASSCF (complete active space SCF). Also often used is Møller–Plesset perturbation theory at various orders (MP2, MP3, MP4). The second-order polarization propagator approximation (SOPPA) is the method of choice for those using the polarization propagator formalism as an alternative approach to study atomic and molecular properties within both regimes, relativistic and nonrelativistic. Finally, there is density functional theory (DFT), which is a very popular method for including electron correlation, particularly for very large systems, but is still in a stage of development of improving the exchange-correlation functionals. These are some of the methods which have been used for calculations of NMR quantities, including intramolecular and intermolecular property surfaces.

The most accurate *ab initio* shielding surfaces for simple molecules have been calculated by Gauss *et al.* using CCSD(T). For example, using large basis sets, they have calculated shieldings at seven different bond distances for diatomic molecules H_2, HF, N_2, CO, and F_2 to find the first and second derivatives of shielding for all nuclei.[83,84] Their results agree with the trends found in the earlier RHF calculations, and their results provide better agreement with experimental temperature dependence and isotope shifts.

Shielding surfaces for more complicated molecules include the variation of the shielding with respect to bond angles and dihedral angles in addition to bond lengths. Shielding surfaces for polyatomic molecules are best expressed in terms of the symmetry coordinates that are the symmetry-adapted linear combinations of bond stretches, bond angles, and dihedral angles, rather than local modes. This is especially advantageous to use for small molecules such as H_2O, NH_3, PH_3, and CH_4, where there is a small number of symmetry coordinates. The first complete analysis of the shielding surface of a polyatomic molecule and the accompanying rovibrational averaging was carried out for ^1H and ^{17}O in H_2O molecule by Fowler and Raynes.[72,73] Later, Raynes *et al.* carried out the quantum-mechanical calculations and complete

analysis of the ^{13}C and ^{1}H shielding surfaces for CH$_4$ and also the rovibrational averaging.[74-76] We did the same for NH$_3$[85] and PH$_3$,[86] including solving numerically for the highly anharmonic vibrational wavefunctions for the umbrella inversion coordinate. A comparison of the shielding surfaces for the central atom in these molecules (H$_2$O, NH$_3$, PH$_3$, CH$_4$,) with respect to the symmetry coordinates reveals similar signs and curvatures. There is a marked difference in the X shielding change with respect to HXH bond angle; however; the minimum in this trace on the shielding surface in H$_2$O is at the equilibrium bond angle, while the minimum occurs at slightly smaller and markedly larger bond angles than equilibrium for NH$_3$ and PH$_3$, respectively,[86] that lead to different overall temperature dependences for the X nuclei when rovibrational averaging is carried out, as described in the following section. These shielding calculations were done at the RHF level. Subsequent correlated calculations reveal very similar shapes of the shielding surfaces.

Correlated calculations for shielding surfaces for all nuclei in H$_2$O have been carried out by Fukui *et al.* using finite field MP3,[87] and by Vaara *et al.*[88] and Raynes *et al.* using MCSCF.[89] The most accurate shielding surface calculations for H$_2$O have been carried out using CCSD(T) by Gauss *et al.*[90] Fukui *et al.* also carried out finite-field MP3 calculations of the shielding surfaces of NH$_3$ and PH$_3$, CH$_4$ and SiH$_4$, as well as H$_2$S, in terms of the symmetry coordinates,[87] but these still do not constitute accurate calculations since their rovibrationally corrected anisotropies do not agree with experimental values. The most accurate shielding surface calculations for H$_2$S have been carried out using CCSD(T) by Gauss *et al.*;[91] they did the same calculations for SO$_2$ and OCS molecules at the same level of theory. The full shielding surfaces with respect to seven symmetry coordinates have been calculated for HC≡CH at the MCSCF level.[92]

The shielding surfaces for ^{13}C and ^{77}Se in CSe$_2$ have been calculated using MCSCF and DFT.[93] Of interest is the result that the derivatives $(\partial\sigma^{Se}/\partial r)_e$ and $(\partial\sigma^{Se}/\partial r')_e$ are roughly equal, which the authors found somewhat surprising, as it means that the effect of change in the bond not directly attached to the observed nucleus may be as important as that in the directly attached bond. This was also found in the case of ^{13}C shieldings in HC≡CH molecule,[92] but not for ^{1}H in this molecule, nor for ^{1}H in the di- or tri-hydrides of the first and second row in the periodic table.[82] The dependence of the shielding on torsion angles (that involve the observed nucleus) has been shown experimentally and theoretically to be the primary determining factor for the dispersion of the ^{13}C chemical shifts in proteins. The ^{13}C chemical shifts of the alanine residues, for example, in a folded protein differ from those of the random coil version of the protein, largely because the torsion angles of the various alanine residues in the folded protein are determined by the secondary and tertiary structure of the folded protein. Theoretical calculations of this torsion angle dependence led to the realization that ^{13}C chemical shifts in proteins are robust indicators of protein structure.[94]

Early reviews of intramolecular shielding surfaces are given in ref. 95 and 96, with direct comparison of the shapes of intermolecular and

intramolecular shielding surfaces, and including shielding surfaces for ^{13}C and ^{15}N in amino acids and proteins.[96] For current annual reviews, consult Section 2.2 Shielding Surfaces and Rovibrational Averaging in the Specialist Periodical Reports on Nuclear Magnetic Resonance published by the Royal Society of Chemistry.[97]

The large errors in DFT calculations of shielding surfaces has been demonstrated in comparison to CCSD(T) calculations of the non-relativistic part in XeF_2 molecule.[98] For ^{19}F shielding, DFT drastically overestimates the correlation effects in this molecule. For molecules containing heavy atoms, there are relativistic contributions to shielding. Here the relativistic corrections to the absolute shielding and shielding anisotropy are very important for both nuclei. For ^{19}F in XeF_2, both the non-relativistic and the relativistic terms are deshielding with increasing bond length, thus relativistic effects further enhance the decrease in shielding compared to that found for ^{19}F in fluorohydrocarbons. On the other hand, for the central atom, Xe, almost full mutual cancellation of the negative non-relativistic and positive relativistic contributions results in small derivatives of the shielding for Xe. The greater sensitivity of the spin–orbit (SO) contribution relative to the scalar relativistic correction to bond stretch in the Xe and F shielding surfaces in XeF_2 has also been noted. In another example, it has been found that the spin–orbit contribution to the ^1H shielding in HI has an opposite distance dependence to the non-relativistic contributions; SO shielding increases with increasing bond length, opposite to the trend for ^{19}F in XeF_2, while the non-relativistic contributions behave as usual for ^1H, decreasing with bond length.[99] Similarly, SO shielding for ^{13}C in CTe_2 increases with increasing bond length and the second derivatives with bond stretch and bending are also positive, but the mixed second derivative with respect to the two bond distances is negative.[100] There has been no systematic study of the signs and magnitudes of the bond-length dependence of the relativistic scalar and SO contributions to shielding as has been done for the non-relativistic shielding.

1.3.3 Rovibrational Averaging. The Connection between the Temperature Dependence in the Zero-density Limit and Isotope Shifts

Rovibrational averaging of shielding is interesting in its own right and is perhaps the most precisely measured among molecular electronic properties. A general discussion of the theoretical and observed effects of rovibrational averaging reveals the ways in which the observed rovibrational effects on all these molecular properties can be understood for individual nearly isolated molecules using the same theoretical framework.[66] In all cases we need the intramolecular potential energy surface in the vicinity of the equilibrium geometry. The PES can be used to solve for the anharmonic vibrational wavefunctions or else its derivatives (force constants up to cubic,

even quartic, may be necessary) may be available either from theoretical calculations or from vibrational spectroscopy. In some cases the quality of the quantum-mechanically calculated potential surface can be good enough to carry out the calculations of the anharmonic vibrational wavefunctions. Then we also need the electronic property surface. This is sometimes close to linear with respect to a displacement coordinate at the equilibrium geometry. In this case, it is the anharmonicity of the PES that provides most of the temperature dependence. The temperature dependence of the dynamic averages of nuclear displacement coordinates coupled with the derivatives of the shielding surface with respect to these coordinates permit the observed temperature dependence to be understood quantitatively. Sometimes, the minimum of the potential energy surface corresponds to a region in the property surface with significant curvature (non-negligible $(\partial^2 P/\partial r^2)_e$, $(\partial^2 P/\partial \theta^2)_e$, …). In this case even using harmonic vibrational wavefunctions can lead to significant temperature dependence. On the other hand, the zero-point vibrational (ZPV) correction to the property may be largely reproduced by harmonic terms only. The isotope effect on molecular electronic properties is treated in the same theoretical framework. The mass dependence of the dynamic averages of nuclear displacement coordinates coupled with the derivatives of the shielding surface combine to provide isotope shifts. The observed temperature dependence of the shielding provides a stringent test of theoretical shielding surface calculations, as do the observed isotope shifts. Reviews with particular emphasis on isotope shifts are given in ref. 101 and 102; for current annual reviews, consult Section 2.3 Isotope Shifts in the Specialist Periodical Reports on Nuclear Magnetic Resonance published by the Royal Society of Chemistry.[97]

Any molecular electronic property P that is a function of nuclear configuration may be expressed as an expansion in terms of the dimensionless normal coordinates

$$P = P_e + \sum_{si} \left(\frac{\partial P}{\partial q_{si}}\right)_e q_{si} + \frac{1}{2} \sum_{si} \sum_{s'i'} \left(\frac{\partial^2 P}{\partial q_{si} \partial q_{s'i'}}\right)_e q_{si}\, q_{s'i'} + \cdots \qquad (1.5)$$

where the subscript e designates the value at the equilibrium configuration, s denotes the sth vibrational mode, and i classifies each of the degenerate vibrations. The observed shielding at a given temperature may thus be written in terms of derivatives of nuclear shielding. The expectation values of the dimensionless normal coordinates should be calculated to at least first order using anharmonic vibrational wavefunctions while it is sufficient to use the zeroth order vibrational wavefunctions to calculate the expectation values of $q_{si}\, q_{s'i'}$. These vibrational state averages can then be weighted according to the populations of these states at a given temperature. Early work expressed the expectation values in terms of force constants up to cubic, and then, rather than a proper statistical weighting by populations, instead used an approximate sum over harmonic states in the high-temperature limit, since this sum could be expressed in closed form with the coth function.[103]

Complete analysis of high-resolution rotational–vibrational spectra of the molecule provides the required molecular constants needed in calculating the expectation values and populations, including the rotational portion (centrifugal distortion).

The observed large temperature dependence of ^{19}F shielding in diatomic molecules F_2 and ClF[103] and CF_4, SiF_4, and BF_3 served as first examples in this analysis.[104] A molecule-dependent mass-dependent transformation relates the dimensionless normal coordinates to the curvilinear internal displacement coordinates such as $(R\text{-}R_e)_{bond}$ and angle deformations. Symmetry dictates that only totally symmetric vibrational modes can contribute to the linear term in eqn (1.5). For T_d AX_4, D_{3h} AX_3, and O_h AX_6, $D_{\infty h}$ AX_2 molecules, there is only one totally symmetric mode; for $C_{\infty v}$ ABX molecules, there are two, involving the two distinct $(R\text{-}R_e)_{bond}$, and for C_{2v} AX_2 and C_{3v} AX_3 molecules, there are two, one involving bond stretches, the other involving angle deformations.[104–106] Consideration of the mass dependence of the derived expressions in diatomic molecules, and in those cases where only bond stretches contribute to the totally symmetric vibrational mode, permitted a derivation of isotope shifts in terms of the same constants as those for the temperature dependence of shielding for polyatomic molecules. This led to an approximate expression that explicitly relates the isotope shift to the fractional change in mass $(m' - m)/m'$,[77,107] and also provided the theoretical basis for the many observed trends in experimental isotope shifts.[108–110] On the other hand, the calculated temperature dependence of A in C_{3v} AX_3 or C_{2v} AX_2 molecules is found to depend on angle deformations as well. A complete treatment of the rovibrational averaging for H_2O and its isotopomers was carried out by Fowler and Raynes,[73] using the *ab initio* shielding surfaces they had calculated at the RHF level. Improved calculations for rovibrational averaging of shielding in H_2O were later carried out using correlated shielding calculations by Vaara *et al.*[88] and by Raynes *et al.*,[89] using RASSCF and MCSCF methods, respectively. The temperature dependence of ^{15}N in NH_3 was found to be very small, and this was due to the opposite temperature dependence arising from the umbrella inversion mode compared to all other modes.[85] Except for the inversion, the shielding surfaces of ^{15}N in NH_3 and ^{31}P in PH_3 are remarkably similar and do scale to one another. But for ^{31}P in PH_3, the temperature dependence contributions coming from various terms reinforce rather than oppose each other, leading to an overall negative temperature dependence (deshielding with increasing temperature).[86]

For diatomic molecules eqn (1.5) reduces to a very simple form and much of our understanding and physical insight about isotope shifts and temperature dependence of shielding was developed by studies of F_2, ClF, N_2, and CO.[103] What are the relative contributions to the temperature dependence observed for shielding of the isolated polyatomic molecule in the gas phase? If we start out with the *ab initio* calculations of the shielding surface, then, to answer this question, the surface calculations and the averaging of the dynamic variables is best carried out in terms of the symmetry

coordinates and normal modes, as in eqn (1.5). However, thinking in terms of local bond stretching and other local displacements involving the observed nucleus permits extension of understanding gained from diatomic molecules and small symmetric molecules to much bigger molecular systems, without carrying out the full surface calculations and rovibrational averaging indicated in eqn (1.5). For nuclei of end atoms such as ^{19}F and ^{1}H in a polyatomic molecule, the local bond stretching internal coordinate turns out to dominate the temperature dependence. This is still true at the highest level of calculations using CCSD(T) for both shielding and potential functions.[83,84,92] This is still the case for ^{19}F in XeF$_2$, even though there are relativistic contributions that make the analysis more complicated.[98] The results for the ^{77}Se on the end atoms in CSe$_2$ are as expected, but $(\partial \sigma^{Se}/\partial r')_e$ is not much smaller than $(\partial \sigma^{Se}/\partial r)_e$.[93] It had been proposed early on that two-bond isotope shifts had two important contributions: (a) the shielding change with respect to the stretch of the remote bond coupled with the mass-dependence of the remote bond length upon isotopic substitution of one of the atoms participating in the bond, (b) the shielding change with respect to the stretch of the local bond coupled with the dependence of this average bond length on a remote mass change, and that (a) was likely more important than (b).[101,102] In other words, observations of 2- and 3-bond isotope shifts are by themselves experimental indicators of significant change in shielding upon stretch of a bond 2 or 3 bonds away from the observed NMR nucleus in the molecule. The $^{74-82}$Se-induced ^{77}Se isotope shifts in CSe$_2$ are well-reproduced by using all first and second derivatives.[93]

The case for centrally located nuclei is more ambiguous. We have already mentioned the various contributions in the cases of ^{17}O, ^{15}N, and ^{31}P in H$_2$O, NH$_3$, and PH$_3$ molecules. For the ^{13}C shielding in HC≡CH, the dominant nuclear motion contribution comes from the bending at "the other" carbon atom with the combined stretching contributions being only 20% of those from bending.[92] The relative importance of first and second derivatives of ^{13}C shielding to the zero-point vibrational contributions and isotope shifts in substituted methanes CF$_n$H$_{4-n}$ has been investigated by Bour *et al.* but this is probably not the last word on these systems since they are unable to reproduce the experimental zero density ^{13}C shifts relative to CH$_4$.[111] The results for ^{13}C in CSe$_2$ are likewise ambiguous, so that the Se mass effects on the ^{13}C spectrum are not as well reproduced as those in the ^{77}Se spectrum.[93] For ^{129}Xe in XeF$_2$, there is a practically negligible (less than 0.1%), slightly negative ZPV correction to σ^{Xe}, that slightly increases only up to a few ppm due to finite temperature contributions. This is partly due to the almost full cancellation of the non-relativistic and relativistic contributions to $\langle \sigma^{Xe}_r \rangle^T$ (the first-order term in the rovibrational contributions arising from the stretch of the bond to the nucleus in question) that results in almost constant vibrational contribution in the whole temperature range. In addition, heavy cancellation takes place between the second-order terms $\langle \sigma^{Xe}_{rr} \rangle^T$ and $\langle \sigma^{Xe}_{rr'} \rangle^T$, thus the $\langle \sigma^{Xe}_{\theta\theta} \rangle^T$ term is mostly responsible for the Xe temperature

dependence (the indices correspond to the contributions to the vibrational corrections from first and second shielding derivatives).[98]

It has been found that it is more efficient to solve directly for the vibrational wavefunctions from quantum-mechanically calculated potential surfaces. This method has been applied to finding zero-point vibrational corrections to the shielding and other properties in HF, H_2O, NH_3, and CH_4,[112] [19]F in 24 fluorohydrocarbons,[113] and also applied to all nuclei in H_2, HF, and H_2O.[114]

1.3.4   Absolute Shielding Scales and Comparison with State-of-the-Art Quantum Calculations

For molecules with larger numbers of atoms, DFT is still the most efficient method of introducing electron correlation, but the absolute errors in DFT calculations cannot be revealed by comparing against experimental chemical shifts because of cancellation of computational errors in taking shielding differences, especially between similar types of molecules. Comparing different functionals against one another in this way actually may lead to wrong conclusions about the usefulness of particular functionals for shielding estimates that may be applied to structural assignments of NMR spectra in condensed phase; we have seen already the quantitative measure of intermolecular effects on shielding that only gas phase experiments reveal. Thus, the practice of comparing a set of calculated shieldings against the chemical shifts measured for the same set of molecules relative to some standard reference does not provide a true test of the quality of the theoretical results. For comparisons of very accurate *ab initio* calculations with experiment (thermal average for the isolated molecule at 300 K), it is necessary to include the zero-point vibrational corrections to obtain $\langle \sigma \rangle^{0K}$ and the additional thermal corrections to obtain $\langle \sigma \rangle^{300K}$. Then one will have the absolute shielding for the nucleus in that specific isolated molecule. These corrections have been carried out by Gauss *et al.* for several nuclear sites in a variety of molecules (molecules with lighter atoms where the relativistic corrections are expected to be small), so as to test the quality of various levels of theory, including DFT, using a variety of functionals, against the gold standard, CCSD(T), and against experiments in the gas phase extrapolated to zero density at 300 K.[115] By doing so, the deficiencies of the DFT methods for shielding calculations have been revealed. In future, incremental improvements in exchange-correlation functionals can be tested by using these large numbers of molecular systems for which the theoretical absolute shieldings $\langle \sigma \rangle^{300K}$ have been ultimately checked against experimental values of $\langle \sigma \rangle^{300K}$. Experimental absolute shieldings for small molecules are obtained by measurements of chemical shifts in gas phase experiments extrapolated to the isolated molecule limit, coupled with the determination of $\langle \sigma \rangle^{300K}$ in at least one standard reference molecule containing the nucleus of interest, derived from high-resolution microwave measurements of the spin-rotation constant. The method of determining from an experimental spin-rotation

constant measured for a particular rovibrational state, the paramagnetic part of the shielding at the equilibrium geometry and adding to this the calculated diamagnetic term at the equilibrium geometry and then making the rovibrational corrections to obtain $\langle\sigma\rangle^{300K}$ for that standard reference molecule has been in use for some time.[30] It continues to be used in current work, on ^{17}O, for example.[88,90] Thus, $\langle\sigma\rangle^{300K}$ data are available for sets of molecules for ^{1}H,[116] for ^{13}C,[117] for ^{15}N,[118] for ^{17}O,[119,120] for ^{19}F,[30,31] for ^{29}Si,[121,122] for ^{31}P,[123] for ^{33}S,[124,125] for ^{77}Se and ^{125}Te.[126] Since accurate chemical shifts between molecules all extrapolated to the zero density limit have been reported for these cases, in future, more accurate values of spin-rotation constants for the standard reference can always be used to improve the reported absolute $\langle\sigma\rangle^{300K}$ values. For example, more accurate values for the standard ^{17}O reference H_2O,[90] ^{19}F reference HF,[83] ^{31}P reference PH_3,[127] ^{33}S reference H_2S and SO_2,[91] have become available. Gauss *et al.* have used experimental values for $\langle\sigma\rangle^{300K}$, a set of values that have been measured in the gas phase in the isolated molecule limit based on the spin-rotation constant of one specific standard molecule among the set, to compare accurately calculated shieldings at the CCSD(T) level and large basis sets and including rovibrational corrections for ^{13}C,[128] for ^{17}O,[129] for ^{19}F,[130] and for ^{15}N and ^{31}P,[131] and finally for benchmarking theoretical calculations against CCSD(T) for these nuclei and also ^{7}Li, ^{27}Al, and ^{33}S in selected molecules.[115]

As reviewed earlier[132] and in Chapter 3 by Jackowski and Garbacz in this book, it is also possible to measure absolute shieldings directly without using a spin-rotation standard reference by using the ratio of resonance frequencies for two nuclei in the same sample, and ultimately a suggestion to use a single standard reference for all nuclei, ^{3}He in the He atom.[133] The proposed new method of shielding measurements neither removes nor solves the problem of bulk susceptibility correction when the helium sample is used as the external standard. On the other hand, any NMR experiment performed for a gaseous compound with the extrapolation of results to the zero-density at 300 K gives immediately the exact value of the shielding constant when the reference used is ^{3}He. This latter method has been applied to the determination of the absolute shieldings $\langle\sigma\rangle^{300K}$ for ^{1}H in several molecules,[116] and for $^{35/37}Cl$ in HCl.[134]

1.4　The Spin–Spin Coupling in the Gas Phase

There are alternative measurements of *J* in isolated molecules: hyperfine data obtained from high resolution molecular beam and microwave spectroscopies, in particular, the parameters c_3 and c_4 yield the complete experimental indirect spin–spin coupling tensor for an isolated molecule in the gas phase,[135,136] but here we consider only the results from gas phase NMR experiments. The general approaches used as described above for shielding apply equally well to other molecular electronic properties, in particular the spin–spin coupling *J*.[66] This NMR quantity does not appear to have the very marked density and temperature dependence in the gas phase

that has been found for shielding. Nevertheless, in 1966, Carr *et al.* observed both a small increase in $J(HD)$ in the proton spectrum with increasing temperature at constant density and a small decrease with increasing density at constant temperature.[137] They were able to account for the temperature dependence of $J(HD)$ in terms of the centrifugal stretching of the HD bond when rotational states are excited as the temperature increased. Theoretical calculations of J as a function of geometry are more difficult than those for shielding since four parts (Fermi-contact, spin-dipolar, orbital diamagnetic, and orbital paramagnetic mechanisms) contribute in the gas phase, each having a different dependence on internal coordinates.

1.4.1 The Density Coefficient of the Spin–Spin Coupling

The first measured second virial coefficient of J coupling in a polyatomic molecule was reported in 1971 for the one-bond $J(^{29}Si^{-19}F)$ in SiF_4 gas.[138] Since then, only a few values of the second virial coefficient J_1 (analogous to σ_1) have been reported. Examples are J_1 for the one-bond couplings $J(^{11}B^{-19}F)$ in BF_3,[24,139] $J(^{13}C^{-19}F)$ in CD_3F,[140] in CH_2F_2,[35] and in CHF_3,[34] $J(^{13}C^{-1}H)$ in CH_2F_2,[35] in CHF_3,[34] in CH_3Br,[46] in CH_3I,[141] and in benzene,[44] $J(^{13}C^{-13}C)$ in $HC{\equiv}CH$,[45] $J(^{13}C^{-15}N)$ in CH_3CN,[41] and $J(Si\text{-}F)$ in $(SiF_3)_2O$.[37] A few J_1 have been reported for two-bond couplings $J(HCF)$ in CHF_3,[34] and CH_2F_2,[35] $J(DCF)$ in CD_3F,[140] $J(HCC)$ in CH_3CN,[41] and for three-bond coupling, J_1 has been reported for $J(HCCN)$ in CH_3CN.[41] Jackowski has reviewed gas phase studies of spin–spin coupling.[142]

1.4.2 The J Surface and the Effects of Rovibrational Averaging

The earliest (1959) theoretical calculation of a J surface is that for the dependence of the 3-bond coupling constant on the dihedral angle by Karplus,[1] that has turned out to be an extremely useful result that applies to the general coupling path $J(X\text{-}B\text{-}C\text{-}Y)$, with nuclei X and Y throughout the periodic table and any intervening atoms B and C. The universal form of the Karplus equation is:

$$J(\phi) = a\cos(2\phi) + b\cos\phi + c \qquad (1.6)$$

with the parameters a, b, c depending on the four atoms in the coupling path. The original work used various rotated ethanic fragments and the valence-bond method, and assumed that the Fermi-contact (FC) mechanism dominated the coupling. It is worth noting that the Karplus equation has remained valid after more than five decades. When the four parts of the coupling rather than just the Fermi contact have been calculated for rotated ethanes,[143] the common assumption that the Fermi-contact term is totally dominant has been confirmed. The derivatives of the orbital paramagnetic and orbital diamagnetic terms are significant but opposite in sign for this

case. It is found that the coefficients in the Karplus equation, when electron correlation is included (*e.g.*, using SOPPA(CCSD) or MCSCF), are in good agreement with coefficients derived from experimental coupling constant data. It is further observed that extending the Fourier series in the Karplus equation to include $\cos(3\phi)$ and $\cos(4\phi)$ terms neither significantly improves the quality of the fit nor significantly changes the values of the other coefficients.

The reduced coupling constant $K(AB) = J(AB) \, 4\pi^2 [h\gamma_A\gamma_B]^{-1}$, the nuclear moment-independent electronic part of the J coupling, is usually considered instead of J itself, so as to be able to compare the sign of the coupling between nuclear pairs throughout the periodic table,[144,145] to compare relative sensitivities to bond displacements from one pair of nuclear sites to another in a variety of molecular systems, or to discuss isotope effects resulting from vibrational averaging.[102,146] The dependence of the one-bond spin–spin coupling on bond length is manifest in observed isotope effects on K, for example $K(DF) \neq K(HF)$ for hydrogen fluoride molecule. This is called a primary isotope effect $= |K(DF)| - |K(HF)|$, arising from isotopic substitution of one of the coupled nuclei. Note that this definition involves the difference between the absolute magnitude of the coupling constant for the heavy minus the light isotopomer. Secondary isotope effects are defined similarly, except that they arise from isotopic substitution of other than the coupled nuclei in the molecule. Occasionally, the magnitudes of secondary isotope effects on K can be larger than the primary isotope effects. This, too, is a manifestation of the K mathematical surface in terms of internal coordinates of the molecule.

A simple example system is of course a diatomic molecule, of which the simplest is the HD molecule. The temperature dependence of $J(HD)$ had been measured from proton resonance studies in the gas phase over a 250-degree temperature range by Beckett and Carr.[147] By fitting these data to the thermal average of eqn (1.5), Raynes and Panteli obtained the first derivative of J with respect to bond extension by neglecting the smaller temperature dependence of the mean square displacement.[148] For the isotopomers of HD, Raynes *et al.* found that the term in the first derivative is mostly responsible for the primary isotope effect on the coupling, with the opposite signed term in the second derivative making a small contribution.[149]

Although there were some earlier calculations at various levels with and without electron correlation, for the HD molecule the highest level of theory, full configuration interaction calculations in the basis set limit, can actually be used. With FCI, an equilibrium value of $J_e(HD) = 41.22$ Hz is obtained in the basis set limit.[150] Adding a calculated zero-point vibrational correction of 1.89 Hz and a temperature correction of 0.20 Hz at 300 K leads to a total calculated spin–spin coupling constant $\langle J_0(HD) \rangle_{FCI}^{300K} = 43.31(5)$ Hz, which is within the error bars of the experimental gas phase NMR value, $\langle J_0(HD) \rangle_{EXPT}^{300K} = 43.26(6)$ Hz, obtained by extrapolating values measured in HD–He mixtures to zero density. These results are the ultimate as far as experiments and theoretical calculations are concerned, but are not very

different from the earlier calculations by Oddershede *et al.* using SOP-PA(CCSD) at 11 R values, that led to a vibrational correction of 1.81 Hz.[151] or the MCSCF calculations that led to a thermally averaged value of 43.15 Hz.[152]

For the HF molecule, CASSCF calculations provide a ZPV correction of 25 Hz and the thermal average $\langle J_0(HF)\rangle^{300K} = 510(10)\,Hz$[153] that compares well to the molecular beam results $\langle J(HF)\rangle_{v=0} = 500(20)\,Hz$.[154] The value at the equilibrium geometry, $J_e(HF)$, and also the bond length dependence are dominated by the Fermi-contact term. On the other hand, in N_2 and CO, the nuclear spin–spin coupling bond length dependence is sharp and largely due to the Fermi-contact term. While the other mechanisms do not show any appreciable geometry dependence, the FC term even changes sign near the equilibrium geometry. This feature, a sharply varying FC term with an inflection point close to equilibrium, gives an explanation for the apparently great importance of non-contact mechanisms for CO and N_2 molecules and possibly also for other multiply bonded systems.[155]

Raynes *et al.* have comprehensively investigated the rovibrational effects on the J couplings in CH_4, using SOPPA(CCSD)[156–158] and MCSCF,[159] to obtain the coupling surfaces in terms of the symmetry coordinates, to obtain vibrational averages of both $J(CH)$ and $J(HCH)$, and to calculate the isotope effects at various temperatures for these spin–spin couplings.[158] They have carried out similarly comprehensive studies for SiH_4.[159,160] There is parallel behavior between respective surfaces of SiH_4 and CH_4 in the reduced couplings. It is not surprising that K values for $^{29}SiH_4$ are generally twice those for $^{13}CH_4$. This is consistent with the observation that the one-bond $K(XF)$ for X in analogous compounds exhibits the same periodicity across the periodic table when plotted against atomic number as does the $|\Psi_{ns}(r=0)|^2$ for the X atom.[161] Furthermore, bending is also relatively more important in SiH_4 than in CH_4. In the total nuclear motion effects, first-order stretching is dominant but there are significant contributions also from the second-order terms in SiH_4.

Raynes *et al.* have also investigated the J surfaces of H_2O[162] and $HC\equiv CH$,[163] at the SOPPA(CCSD) level, calculating all nuclear motion effects. Other calculations on the water molecule surfaces, using MCSCF,[164] find only small differences when compared to the SOPPA(CCSD). All the ZPV corrections discussed above were calculated assuming small-amplitude nuclear motions. For large-amplitude nuclear motions, other approaches, such as statistical averaging over conformational isomers (for 3-bond coupling across a dihedral angle, for example) and molecular dynamics, are needed for a meaningful comparison with experimental measurements. For NH_3, it is found that the umbrella inversion mode has significant contributions to the dynamic averaging of the coupling constants,[165] just as had been found for the dynamic averaging of ^{15}N shielding in this molecule.[85]

Stanton *et al.* have carried out benchmark calculations of all J surfaces (for all one-, two-, and three-bond couplings) in $HC\equiv CH$, $H_2C=CH_2$, CH_3CH_3, and cyclopropane, including all four mechanisms for each, and using coupled cluster theory to CCSD level with large uncontracted basis sets for

accurate description of the Fermi-contact contribution that dominates in these molecules.[166] They also carried out vibrational averaging to second order in the normal coordinates and evaluated the zero-point vibrational average using CCSD for the anharmonic potential surface. They found that two-bond CCH couplings are the most affected by vibrational averaging. The relative importance of first and second derivatives of one- and two-bond J couplings to the zero-point vibrational contributions and isotope effects in substituted methanes CF_nH_{4-n} have been investigated by Bour *et al.*[111] The uniformly positive values of the first derivatives of the one-bond $J(CH)$ with respect to the CH bond stretch in CH_4 and $H_2C=CH_2$ likewise accounts for the generally negative CH primary isotope effect in these molecules, just as found in alkyl sites in general.[146]

The performance of various exchange-correlation functionals for the Fermi-contact contribution to J varies from one molecular system to another in the same series,[167] therefore DFT would not be a method of choice for J calculations. Nevertheless, DFT calculations of the dependence of one-bond and two-bond J couplings on normal coordinates have been carried out,[168] particularly calculations of one-bond coupling including relativistic corrections, for example in the dependence of $J(^{31}P–^{31}P)$ in H_2P-PH_2 and H_2P-PF_2 molecules on the dihedral angle between the bisectors of the two $\angle HPH$, or the $\angle HPH$ and the $\angle FPF$.[169] Since biphosphines are not fixed in a particular conformation, observations of $J(^{31}P–^{31}P)_{iso}$ represent conformationally averaged values. It has been suggested that one practical strategy for J calculations would be for J at the equilibrium geometry to be calculated accurately using coupled cluster theory, then use DFT to calculate the vibrational corrections.[170]

A study of the general trends in primary and secondary isotope effects on spin–spin coupling in small molecules can reveal interesting information about general trends in spin coupling surfaces.[102,146] Primary isotope effects on reduced one-bond coupling, *e.g.*, $|K(D_2)| - |K(HD)|$ is negative for hydrogen molecule, are generally negative for CH in alkyl sites and SiH in silyl sites, negative for SnH in $SnH_{4-n}D_n$, for SnH in $[SnH_{3-n}D_n]^+$, for PH in $[PH_{4-n}D_n]^+$, for $P^{(V)}H$ in $H_2P(O)OH$ and for other similar P sites.[102] In these molecules the main electronic factor that is responsible for the primary isotope effect on K is the first derivative $(\partial K/\partial r)_e$. Since the mean bond length in the heavy isotopomer is shorter than that in the light isotopomer, the negative isotope effects on K in these cases correspond to positive $(\partial K/\partial r)_e$. In other words, the reduced spin–spin coupling increases with increasing bond length in all these systems. On the other hand, the primary isotope effect is positive for HF, and positive for NH in $NH_{3-n}D_n$, for $P^{(III)}H$ in $PH_{3-n}D_n$, for $[PH_{2-n}D_n]^-$, for SeH in $SeH_{2-n}D_n$ and for SnH in $[SnH_{3-n}D_n]^-$. The positive isotope effects on K in these cases correspond to negative $(\partial K/\partial r)_e$ where one of the coupled nuclei is an atom with one or more lone pairs. The lone pair on A is known to be responsible for negative contributions to the reduced coupling $K(AH)$; apparently it is also the lone pair which is responsible for the greater sensitivity of the reduced coupling to

bond extension and for the negative sign of $(\partial K/\partial r)_e$. See Table 3 in ref. 102 for contrasting examples with and without lone pairs and ref. 146 for the rationalization of these trends in terms of the Fermi-contact term.

1.5 Spin–Lattice Relaxation in the Gas Phase. Cross-sections for Angular Momentum Transfer and Molecular Reorientation in the Binary Collision Limit

Spin lattice relaxation in the gas phase provides qualitatively different information from that in condensed fluid phases in many ways; different relaxation mechanisms dominate and interpretation of the experimental relaxation times provide different types of information about the system. Since the intermolecular dynamics in the gas phase can be modeled more accurately (using well-established mathematical theory of non-uniform gases) than in the liquid phase, the gas phase provides critical tests of relaxation theories, permits quantitative separation of two or more contributing mechanisms, and provides a direct connection to intermolecular potential functions.[3] Collisions that do not reorient the molecule containing the nuclear spins make no contribution to relaxation of spin magnetizations. This is the reason that T_1 measurements inherently provide a valuable source of information on the anisotropy of the intermolecular interaction or serve as a sensitive test of anisotropy of proposed *ab initio* or semi-empirical potential energy surfaces.

As a function of gas density, ρ, T_1 is long at very low densities for which the collision frequency is very low (where T_1 is inversely proportional to the gas density, the reciprocal density regime), passes through a characteristic minimum corresponding to a matching between the spin-precession frequency and the collision frequency, then passes into a regime in which T_1 increases linearly with gas density. Early gas phase studies, particularly in the vicinity of the T_1 minimum, are reviewed in ref. 171 and 172. For the purposes of determining classical cross-sections in a pure gas, the regime of densities that is appropriate to study is that for which T_1 is proportional to the density of the gas, sometimes called the "extreme narrowing limit" (see also ref. 3). In the following sections, we restrict our discussion to this linear-density regime. For a discussion of the lower density regions where different relaxation rates for different nuclear spin symmetry species may be expected and systems where a quantum scattering treatment is required, see Armstrong's review in ref. 172.

1.5.1 Temperature-dependent Classical Cross-Sections from Gas Phase Studies

In 1966, Roy Gordon developed a kinetic theory for nuclear spin relaxation in dilute gases and mixtures of gases,[173] employing classical mechanics for the

molecular translational and rotational motion, assuming binary collisions, and no correlation between the effects of successive binary collisions, resulting in expressions relating the measured spin relaxation times in the linear-density regime to two cross-sections that could be calculated for any intermolecular potential having angle-dependent terms. The spin relaxation times in a dilute gas are found to depend only on the net changes produced by collisions in the molecular rotational angular momentum vector but not on the details of the trajectory during a collision. This permits the description of relaxation in the dilute gas in terms of cross-sections. For the quadrupolar relaxation mechanism,

$$T_{1Q} = \frac{160I^2(2I-1)}{3(2I+3)}\left(\frac{\hbar}{eqQ}\right)^2 \rho\bar{v}\sigma_{\theta,2} \tag{1.7}$$

$eqQ/\hbar$ is the nuclear quadrupole coupling constant, ρ is the number density of the collision partner measured in amagat (2.687×10^{25} molecules m^{-3}), and $\bar{v}$ is the mean relative speed that is given by $(8k_BT/\pi\mu)^{1/2}$ with μ the reduced mass of the colliding pair. The electronic coupling affects the populations of the nuclear magnetic spin states of a nucleus with $I>1/2$ since the magnetic moment of the nucleus is directed along the axis of the nuclear electric charge distribution of this nucleus. The subscript in the cross-section signifies the connection to the $P_2(\cos\theta)$ autocorrelation function, where θ is the angle between the molecular rotational angular momentum vector of A before and after a collision with B.

$$\int_0^\infty \langle P_2[\mathbf{u}(0)\cdot\mathbf{u}(t)]\rangle \mathrm{d}t = \frac{1}{4}\left[\rho\bar{v}\sigma_{\theta,2}\right]^{-1} \tag{1.8}$$

The same cross-section $\sigma_{\theta,2}$ is involved in the dipole–dipole (DD) relaxation mechanism (for like spins),[173]

$$T_{1DD} = \frac{2}{\gamma^4\hbar^2I(I+1)\langle r^{-3}\rangle^2}\rho\bar{v}\sigma_{\theta,2} \tag{1.9}$$

(For the relaxation of the I spin by dipolar coupling to the unlike I' spin, we replace γ^4 by $(\gamma'\gamma)^2$ and 2 by 3.)

Nuclear spin relaxation can also be affected by the molecular rotation when a magnetic coupling exists between the nuclear magnetic moment and the magnetic moment associated with the molecular rotation. The spin-rotation (SR) mechanism is important for nuclei with a spherical charge distribution (spin $I=1/2$). The spin-rotation relaxation mechanism involves a different cross-section, σ_J.[173]

$$T_{1,\mathrm{SR}} = \frac{3}{2C_{\mathrm{eff}}^2\langle J(J+1)\rangle}\rho\bar{v}\sigma_J \tag{1.10}$$

These relations can be applied when the following assumptions hold: (a) The Larmor frequency is small compared with the collision frequency. (b) The duration of a collision is short compared with the average time between

collisions. (c) The interactions among the collision partners do not significantly influence their collisions with the observed molecule. (d) Bound states between the observed molecule and the collision partner have no significant effect on the spin relaxation.

These two relaxation cross-sections are among the 45 collision cross-sections that can be defined in a general formalism and calculated from a known or proposed intermolecular potential function. In order to facilitate a comparison among related information that can be obtained from NMR, depolarized Rayleigh light scattering, microwave non-resonant absorption, transport properties, transport coefficients in the presence of electric or magnetic fields, it is necessary to have an unambiguous yet physically meaningful definition of a collision cross-section for the process being studied. For example, the cross-sections obtained by studying the pressure broadening of the depolarized Rayleigh light scattering spectrum turns out to be the same cross-section as that which can be obtained from NMR relaxation by the quadrupolar mechanism. McCourt and co-workers provide a detailed derivation of the collision cross-sections related to the transport and relaxation properties that are currently used in testing non-reactive potential surfaces.[174,175] From the Boltzmann equation, the Chapman–Enskog procedure[176] can be used to obtain classical definitions of the kinetic theory cross-sections. The nomenclature used to label the collision cross-sections specifies the nature of the collisional process that contributes to the phenomenon. In general, a collision or effective cross-section is written in terms of indices that represent the pre-collisional and post-collisional tensorial ranks or powers of the microscopic polarizations that are coupled and also label which collision partner the polarizations belong to. When the pre- and post-collisional values are identical and changes in only one partner are relevant (in NMR relaxation we observe only one of the collision partners at a time), the cross-section can be abbreviated; $\mathfrak{S}(pqst|A)_{AB}$, for example, is the cross-section for molecule A in the collision of A with B. The index p denotes the p-fold tensor product of the reduced peculiar velocity $\mathbf{W} = (m/2k_BT)^{1/2}\mathbf{v}$ of molecule A, q denotes the tensorial rank in the molecular angular momentum $\mathbf{J}$ for molecule A. The s and t indices denote the scalar dependencies of the cross-section on the translational and reduced rotational energy of molecule A. For example, the cross-section for diffusion is $\mathfrak{S}(1000|A)_{AB}$ and the shear viscosity cross-section is $\mathfrak{S}(2000|A)_{AB}$. For spin–lattice relaxation T_1, $p = 0$, $s = 0$, $t = 0$ since the relaxation cross-sections have a dependence only on the molecular rotational angular momentum $\mathbf{J}$. Liu and McCourt demonstrated the connection between the reorientation collision cross-section expressions arising in NMR relaxation in the gas phase when described from the point of view of kinetic theory and from the point of view of traditional correlation function theory.[177] Thus, the following are identified:

$$\mathfrak{S}(0100|A)_{AB} \equiv \sigma_J \quad \text{and} \quad \mathfrak{S}'(0\hat{2}00|A)_{AB} \equiv \sigma_{\theta,2} \tag{1.11}$$

Intramolecular dipole–dipole, chemical shift anisotropy, and electric quadrupolar relaxation rates obtained in the gas phase all provide the

cross-section $\mathfrak{S}'(0\hat{2}00|A)_{AB}$. The hat symbol over the tensorial rank 2 indicates the use of normalized angular momentum, just as in Gordon's derivation. The prime means this is the "self-only" part which has no dependence upon the collision partner except as introduced *via* the intermolecular potential and *via* the number density of the collision partner. Molecular reorientation in classical language corresponds to a change in the quantum number M_J without a change in the quantum number J. When the spacing between J levels is large (as in H_2 molecule) quantum scattering is the appropriate description of the collision events, but the classical limit for rotation is easily satisfied for most molecular systems. Spin-rotation relaxation rates in the gas phase provide the cross-section for changes in the molecular rotational angular momentum quantum number J of the observed molecule A upon collisions (*i.e.*, in classical terms, a change in the molecule's rotational energy, *i.e.*, molecular rotational energy transfer). Thus, the cross-section $\mathfrak{S}(0100|A)_{AB}$ is also known as σ_J. Thus, eqn (1.10) can also be written as

$$T_1 = \frac{3}{2C_{eff}^2 \langle J(J+1) \rangle} \rho \bar{v} \mathfrak{S}(0100|A)_{AB} \tag{1.12}$$

For a linear molecule C_{eff} is the perpendicular component of the spin-rotation tensor,[173]

$$C_{eff}^2 = C_{\perp}^2 \quad \text{and} \quad \langle J(J+1) \rangle = \frac{2I_0}{k_B T} \tag{1.13}$$

For a nucleus, say ^{19}F or ^1H, in a spherical top such as CF_4, CH_4, SiF_4, SF_6, SeF_6, TeF_6,[178]

$$C_{eff}^2 = \left[\frac{1}{3} \left(C_{\|} + 2C_{\perp} \right) \right]^2 + \frac{4}{45} \left[C_{\|} - C_{\perp} \right]^2 \quad \text{and} \quad \langle J(J+1) \rangle = \frac{3I_0}{k_B T} \tag{1.14}$$

By using more than one isotope it is possible to determine both cross-sections. For example, the ^{15}N spin in the $^{15}N_2$ molecule in the gas phase is completely dominated by the spin-rotation mechanism, so the measurements of T_1 as a function of temperature for $^{15}N_2$ in a mixture of $^{15}N_2$ and Kr can provide the cross-section $\mathfrak{S}(0100|N_2)_{N2\text{-}Kr}$. On the other hand, the ^{14}N spin in the $^{14}N_2$ molecule in the gas phase is completely dominated by the nuclear quadrupolar mechanism, so the measurements of T_1 for $^{14}N_2$ in a mixture of $^{14}N_2$ and Kr can provide the cross-section $\mathfrak{S}'(0200|N_2)_{N2\text{-}Kr}$ as a function of temperature.

When two or more relaxation mechanisms contribute to T_1, it is necessary to separately determine the individual relaxation rates and analyze them individually so as to obtain the relaxation cross-sections that may be compared with those from classical trajectory calculations. In what follows, we will consider each relaxation mechanism in turn. Fortunately, there are many experimental examples where one particular mechanism dominates over all others in the range of gas densities and temperatures studied. Thus, we may characterize the temperature and density dependence of the

relaxation rate arising from that specific mechanism with the same precision as the original data.

1.5.2 Spin-rotation Mechanism

We restrict our discussion to the density regime in which T_1 is proportional to the density of the gas. For several pure gases in which relaxation has been found to be dominated by the spin-rotation mechanism, (T_1/ρ) is found experimentally to be consistent with the power law

$$(T_1/\rho)_{\text{lin}} \propto T^n \tag{1.15}$$

where n is negative; that may be written as

$$\left(\frac{T_1}{\rho}\right)_{\text{lin},T} = \left(\frac{T_1}{\rho}\right)_{\text{lin},300\,\text{K}} \left(\frac{T}{300}\right)^n \tag{1.16}$$

Thus, all measured T_1 values in the pure gas can be characterized by two quantities, $(T_1/\rho)_{\text{lin}}$ at some reference temperature, say 300 K, and the power n; *i.e.*, these two numbers will reproduce the results of every experimental T_1 measurement in the linear-density regime at any temperature in the range of temperatures for which n was fitted. In Table 1.1 we provide these quantities in eqn (1.16) for various pure gases.[179,180–186] In addition ^{19}F spin-rotation relaxation in WF_6, MoF_6, and UF_6 gases have been studied.[187] It is said that the signature of the spin-rotation mechanism is that T_1 has a temperature dependence close to $T^{-1.5}$. We can see in Table 1.1 for the pure gases that this is indeed the case. In eqn (1.10), we note that the explicit T^{-1} arising from the average rotational angular momentum square gives the spin-rotation relaxation rate a steep temperature dependence, while $\bar{v} = (8k_BT/\pi\mu)^{1/2}$ appears in expressions for all T_1 mechanisms in the linear density regime, and the cross-section σ_J itself has a temperature dependence with a power close to -1.

Table 1.1 Characteristics of spin-rotation relaxation for various nuclei in linear and spherical top molecules.

Nucleus	Pure gas	$(T_1/\rho)_{\text{lin},300\,\text{K}}$ ms amagat^{-1}	n	T range, K	Ref.
[13]C	CO	1.231(30)	−1.32(3)	230–420	179
[13]C	CO_2	21.6(5)	−1.51(5)	290–400	180
[13]C	CH_4	10.2(5)	−1.43(2)	230–400	181
[15]N	[15]N_2	2.23(6)	−1.20(3)	215–400	182
[15]N	[15]N[15]NO end	100.5(19)	−1.417(14)	240–400	183
[15]N	[15]N[15]NO cen	54.0(11)	−1.417(14)	240–400	183
[19]F	SF_6	2.132(23)	−1.75(2)	290–400	184
[19]F	SeF_6	3.21(7)	−1.97(5)	310–400	185
[19]F	TeF_6	10.03(10)	−1.82(2)	310–400	185
[19]F	CF_4	1.948(39)	−1.41(2)	210–400	186
[1]H	CH_4	20.2(4)	−1.40(3)	230–400	181

In a mixture of gases A and B, the spin-rotation relaxation times of a nucleus in molecule A in the extreme narrowing limit are additive.[173]

$$T_1(A) = \left(\frac{T_1}{\rho}\right)_{\text{lin},A-A} \rho_A + \left(\frac{T_1}{\rho}\right)_{\text{lin},A-B} \rho_B \qquad (1.17)$$

This additivity of course depends on the neglect of correlations between the effects of successive collisions, as well as on the assumption of binary collisions.

The values characterizing the relaxation of the spin in the molecule (listed in columns 3–4 of Table 1.1) infinitely dilute in a buffer gas (including the following gases: Ar, Kr, Xe, N_2, CO, CO_2, HCl, CH_4, CF_4, SF_6) are also provided in the same references as given in Table 1.1. The cross-section for rotational angular momentum transfer for an observed target molecule by a collision partner is uniquely determined by the details of the anisotropy of the intermolecular potential. Nevertheless, there are general trends in the observations at room temperature across the large number of collision pairs included in ref. 179–186. A physically intuitive simple model provides a comparison between the cross-sections for this wide range of buffer gases and proposes that the efficiency for rotational angular momentum transfer for a target molecule upon collision with various molecules may be thought of as a product of three factors: the anisotropy of the shape of the target molecule, the electronic factors that depend largely on electric polarizabilities and electronic moments of the target and projectile molecules, and a kinematic factor involving molecular diameters, moments of inertia and reduced mass.[188]

1.5.3   Quadrupolar Mechanism

When the nucleus has spin $I > 1/2$, then the quadrupolar mechanism may dominate the relaxation. We consider here the case when the nucleus is in a molecule so that the electric field gradient at the nucleus is an intrinsic molecular electronic property. (In Section 1.5.7 we will consider a transient quadrupole coupling arising from the binary collision itself, an electric field gradient arising from the intermolecular interaction as in the case of ^{131}Xe or ^{83}Kr in the rare gas.) The ^{14}N in $^{14}N_2$ and the end ^{14}N in NNO have been found to relax nearly entirely by the quadrupolar mechanism,[189,190] which permits the characterization of quadrupolar relaxation cross-sections $\mathfrak{S}'(0\hat{2}00|A)_{AB}$ or $\sigma_{\theta,2}$ in the gas phase. The ^{17}O relaxation has been studied and is likewise dominated by the quadrupolar mechanism.[191] Just as for spin-rotation relaxation, we find experimentally that the temperature dependence for quadrupolar relaxation can be described in the form of a power law. Table 1.2 shows the examples for ^{14}N; the quantities are the ones analogous to the quantities in eqn (1.16).

Once again, in a mixture of gases A and B, the quadrupolar relaxation times of a nucleus in molecule A in the extreme narrowing limit are additive,[173] just as in eqn (1.17), so that $(T_1/\rho)_{\text{lin},A-B}$ provides the cross-sections

Table 1.2   Characteristics of quadrupolar relaxation for ^{14}N nuclei in linear molecules.

Nucleus	Pure gas	$(T_1/\rho)_{lin}$ at 300 K ms amagat^{-1}	n	T range, K	Ref.
^{14}N	^{14}N$_2$	0.050(3)	−0.17(2)	225–405	189
^{14}N	^{14}N^{14}NO (end)	4.92(12)	−0.35(4)	265–400	190

for molecule A in collision with B. The cross-section $\sigma_{\theta,2}$ ranges from 29.6(9) Å^2 to 73(2) Å^2 and has a temperature dependence close to −1, ranging from −0.63(4) to −0.91(6) for ^{14}N$_2$ with the 10 different collision partners.[189] From the end ^{14}N nucleus in NNO, we obtain the cross-section that ranges from 43.0(19) Å^2 to 99.4(28) Å^2 and has a temperature dependence close to −1, ranging from −0.66(6) to −0.95(4), for NNO with 10 different collision partners.[190] Of course, the cross-section is a property of the molecule in a collision pair and does not depend on which of its nuclei has been used for the relaxation measurement. In the case of NNO, the end nitrogen provides a more precise determination of the cross-section since the middle nitrogen has a smaller quadrupole coupling constant and therefore the quadrupolar relaxation of the center ^{14}N does not dominate the relaxation rate.

1.5.4   Intramolecular Dipole–Dipole Mechanism

The intramolecular dipolar mechanism is a very significant relaxation mechanism in the liquid phase, but is not so important in the gas phase. Even for ^{1}H in CH$_4$ gas, with a short C–H bond, the intramolecular dipolar mechanism is only a very minor contributor; the ^{1}H T_1 has a temperature dependence of $T^{-1.40(3)}$, typical of spin-rotation relaxation, whereas the intramolecular dipolar mechanism is expected to behave roughly as $T^{-0.5}$. Although the intramolecular dipolar relaxation rate may become important at very low temperatures, at temperatures close to room temperature it contributes very little. Therefore, when attempting to determine cross-sections for molecular reorientation, $\sigma_{\theta,2}$, it is better to use a quadrupolar nucleus and obtain the cross-section from its T_1. The intramolecular dipolar mechanism is important for H$_2$ molecule, but H$_2$ relaxation cannot be treated classically (see Section 1.5.10); it is also important for ^{1}H relaxation in HCl molecule with Ar, which has to be treated at least semi-classically.[192]

1.5.5   Chemical Shift Anisotropy Mechanism

The relaxation rate for the chemical shift anisotropy (CSA) mechanism is proportional to the square of the magnetic field strength and the chemical shift anisotropy. In an axial case,

$$T_{1,\text{CSA}} = \frac{15}{2\gamma^2 B_0^2 (\sigma_\| - \sigma_\perp)^2} \rho \bar{v} \sigma_{\theta,2} \tag{1.18}$$

This mechanism could become dominant in nuclei with large chemical shift ranges, and in bonding situations that produce large shielding anisotropies, and of course at high fields. For ^{77}Se in CSe_2 gas, both the spin-rotation and the chemical shift anisotropy should be significant relaxation mechanisms, similarly for ^{129}Xe in XeF_2 gas, but not for ^{13}C in ^{13}CO where the CSA is not large enough, so spin-rotation mechanism dominates in the latter. The dependence of the CSA relaxation rate on $B_0{}^2$ means that multiple field studies will allow its determination even when it is not the dominant mechanism, as described below.

1.5.6   Relaxation Rates Add When Two or More Mechanisms are Operative

When the electric quadrupole coupling constant is not very large, then the quadrupolar mechanism is no longer dominant. Competing spin-rotation and quadrupolar mechanisms have been found for the ^{2}D in CD_4[193] and for the middle ^{14}N in NNO.[190] In these cases, the relaxation rates add

$$\left(\frac{\rho}{T_1}\right)_{lin} = \left(\frac{\rho}{T_1}\right)_{lin,SR} + \left(\frac{\rho}{T_1}\right)_{lin,Q} \tag{1.19}$$

Other less important mechanisms for these gases are the chemical shift anisotropy, intramolecular dipolar, and intermolecular dipolar mechanisms. For ^{2}H in CD_4, the spin-rotation mechanism is found to comprise an average of 7% of the total relaxation rate and ranges from 6 to 8% for individual buffer gases.[193] For the middle ^{14}N in NNO the spin-rotation is competitive with the quadrupolar relaxation due to the smaller electric field gradient for the middle N in this molecule, so that any errors in the subtracted SR relaxation rate leave errors in the deduced quadrupolar relaxation rate.[190] We consider other cases of competing relaxation mechanisms in Sections 1.5.8 and 1.5.10.

1.5.7   Intermolecular Dipolar, Quadrupolar, Spin-rotation, and Chemical Shift Anisotropy Mechanism

The primary relaxation mechanisms for rare gas pairs are intermolecular. Whereas relaxation mechanisms we have discussed in the preceding sections depend on intramolecular quantities (r, q, $\Delta\sigma$, or C), in the case of the rare gases the collision pair generates the corresponding intermolecular quantities: the dipole–dipole interaction is between the pair undergoing binary collision. An electric field gradient is induced by the intermolecular interaction during a collision, thereby producing a transient electric quadrupole coupling. The intermolecular shielding in a rare gas pair is an anisotropic tensor. A spin-rotation coupling is generated by an intermolecular pair. For ^{3}He relaxation the intermolecular dipolar mechanism dominates

since the other intermolecular mechanisms depend on electronic quantities that correlate with the electric polarizability of the rare gas atoms which, for ³He atoms, is too small to generate a large enough spin-rotation coupling, or intermolecular anisotropic shielding, to compete favorably with the intermolecular dipolar mechanism. On the other hand, ¹²⁹Xe has a well-characterized distance-dependent shielding anisotropy and spin-rotation tensor in the Xe–Xe collision pair that makes the spin-rotation and chemical shift anisotropy mechanism significant in pure ¹²⁹Xe gas. For quadrupolar nuclei ⁸³Kr and ¹³¹Xe, the transient electric field gradient created by the collision pair can provide a quadrupolar relaxation mechanism. Since, by their nature, these intermolecular relaxation mechanisms are less effective than intramolecular ones, collisions with the walls can become relatively important, especially at low densities. Thus, for applications that depend on maintaining the hyperpolarization of rare gases (such as ³He, ⁸³Kr, ¹²⁹Xe) for long times, considerable effort has been expended in preparing surface coatings that render the surface collisions less effective for spin relaxation (such as by eliminating paramagnetic sites from the container surface, which we will consider no further). For those applications, very long relaxation times are desirable since they allow users to polarize the rare gas sample prior to and in a different location than the actual experiment. Excluding surface effects, relaxation rates by any of the intermolecular mechanisms mentioned above should increase linearly with the number density.

The thermally averaged ³He intermolecular dipolar relaxation rate for a pair of colliding fermions such as for ³He in He gas has been derived by Happer *et al.*[194] The expression is the same form as was derived in 1973 by Shizgal[195] and also by Richards *et al.*,[196] although arrived at *via* different routes. Numerical calculations for temperatures from 0.1 to 550 K give a relaxation time increasing with temperature; T_{1DD} is 74.4 h for a He density of 10 amagat at room temperature.[194]

The relaxation rate of ¹²⁹Xe in xenon gas has been investigated precisely and comprehensively by Moudrakovski *et al.*,[197] under various conditions of density, temperature, and magnetic field strengths. The density dependence of the relaxation rate is linear with density up to 160 amagat, as expected for any intermolecular mechanism. However, it begins to exhibit a different behavior at lower densities, particularly below 20 amagat. The authors attribute this to wall effects beginning to be competitive and ultimately becoming dominant at 3 amagat (more about this low-density regime below). By studying different isotopic compositions (natural abundance and ¹³¹Xe-depleted xenon gas) they established experimentally that the scalar relaxation of the second kind arising from the collisions of ¹²⁹Xe with ¹³¹Xe (the latter relaxing *via* an intermolecular quadrupolar mechanism) was not significant. By using different B_0 fields, the authors established that $[T_{1\rho}]^{-1}$ gives a straight-line plot against B_0^2 with an intercept that is field-independent. Both the field-dependent part and the field-independent part are found to be directly proportional to density, using only samples that are

40 amagat or greater. The authors arrived at the conclusion that at least two intermolecular mechanisms are very significant: spin-rotation (originally suggested by Torrey in 1963)[198] and chemical shift anisotropy. The spin-rotation mechanism is field-independent and the CSA mechanism goes as $B_0{}^2$; they are expected to have very different temperature dependences. The authors were able to characterize each of these relaxation mechanisms separately. They also carried out a theoretical calculation of the spin-rotation relaxation rate $[T_{1\rho}]^{-1}$ as a function of temperature, which gave good agreement with the experimental temperature dependence of the field-independent part.

The low-density regime in ^{129}Xe relaxation was studied further by Walker *et al.*[199] and by Saam *et al.*[200,201] These authors find that at Xe densities below 14 amagat, not only wall mechanisms are responsible for ^{129}Xe relaxation. They propose that persistent (as opposed to transient) Xe_2 dimers, or van der Waals molecules (constituting about 1–3% of the xenon in 1 amagat of pure xenon gas at room temperature in two different estimates[200,202]), contribute to the relaxation. The Xe_2 dimer is a well-known molecular species, has a well depth of 282 K, deep enough to contain 25 or 26 vibrational levels and many rotational states that provide high-resolution lines in vacuum ultraviolet spectra observed for transitions including vibrational quantum numbers $\nu = 0$ to 9 in the ground electronic state.[203] They investigated this mechanism by means of introducing other buffer gases (He, Ar, or N_2) that provide third-body collisions that can cause the break-up of the Xe_2 dimer. The behavior of the relaxation as a function of concentration of the buffer gas supports this model. In other words, ^{129}Xe spin relaxation in Xe_2 molecules that persist at low densities (fewer collisions with third bodies) is responsible for some of the relaxation previously attributed entirely to wall effects. To calculate the field-dependent CSA relaxation rate over the entire density range for which experimental data are available ($\sim$1 amagat and >20 amagat), Vaara *et al.*[202] used their *ab initio* Xe–Xe shielding function that had given a good account of the shielding second virial quantity $\sigma_1(T)$,[53] and assumed pairwise additivity for the instantaneous Xe clusters in MD simulations. The simulations provide time-correlation functions from which spectral density functions could be obtained and then $(T_1)^{-1}$. Vaara *et al.* find that the relativistic effects on the calculated shielding anisotropy lead to much steeper change with distance at R values below the equilibrium Xe–Xe distance than their non-relativistic counterparts. Good agreement was found with the results of Moudrakovski *et al.* for all densities >20 amagat[197] and Saam *et al.* for $\sim$1 amagat[201] for pure Xe. They did not carry out MD simulations for gases containing third bodies like N_2 or Ar at the intermediate low-density regimes $1 < \rho < 14$ amagat for which experiments also exist.

The intermolecular quadrupolar mechanism in the gas phase was first observed by Brinkmann *et al.* for ^{131}Xe in 1962 at 298 K and 0.76 T magnetic field strength,[204] and much later, also for ^{83}Kr for gas densities 25–156 amagat at 300 K.[205] They find that $[T_{1\rho}]^{-1}$ was 0.0392 and

0.00213 (s amagat)$^{-1}$ for ^{131}Xe and ^{83}Kr in the pure gases, respectively. The intermolecular relaxation rate can be written as

$$\frac{1}{T_1} = \frac{3(2I+3)}{160I^2(2I-1)}\left(\frac{eqQ}{\hbar}\right)^2 \rho\frac{d^4}{\bar{v}}F\left(\frac{V}{k_BT}\right) \tag{1.20}$$

where d is a characteristic length of the interaction and $F(V/k_BT)\cdot\pi d^2$ is an effective cross-section, where $F(V/k_BT)$ is the collision efficiency that depends on the intermolecular potential function V and temperature, of course. Parallel to the case of ^{129}Xe, the high-density mechanism is the transient electric field gradient created during binary collisions, but later studies including much lower densities by Meersmann *et al.* suggest that in lower densities third-body break-up of stable dimer molecules possessing electric field gradients characteristic of Xe_2 or Kr_2 diatomic molecules is the likely operative mechanism, in addition to wall effects.[206,207] Meersmann *et al.* also confirm in the presence of buffer gases the additivity of $[T_1]^{-1}$,[207]

$$[T_1(A)]^{-1} = \left(\frac{1}{T_1\rho}\right)_{\text{lin},A-A}\rho_A + \left(\frac{1}{T_1\rho}\right)_{\text{lin},A-B}\rho_B + \left(\frac{1}{T_1}\right)_{\text{int}} \tag{1.21}$$

and the additional density-independent intercept (third term in eqn (1.21)) that results from a combination of Kr-surface interactions and the formation of ^{83}Kr$_2$ van der Waals dimers.[207,208]

1.5.8 Intermolecular Nuclear Spin Dipole Electron Spin Dipole Mechanism, Spin Relaxation in the Presence of O_2

An instance in which the intermolecular dipolar mechanism could become dominant for a nucleus in a molecule is in the case of a nuclear spin dipole interacting with an electron spin dipole on the collision partner. This is indeed the case when the collision partner is an O_2 or an NO molecule. The theoretical limit for a hard sphere potential at the high translational energy limit, in the zero-magnetic field limit ($\omega = 0$) is known from earlier work,[209,210]

$$\left(\frac{1}{T_1^{DD}}\right)_{\text{theor limit}} = \frac{16}{3}S(S+1)\gamma_I^2\gamma_S^2\frac{\hbar^2}{d^2}\left(\frac{\pi\mu}{8k_BT}\right)^{1/2}N_S \tag{1.22}$$

where πd^2 is the hard sphere cross-section, as before, $\bar{v}$ is the mean relative speed that is given by $(8k_BT/\pi\mu)^{1/2}$ and $\langle S(S+1)\rangle$ is taken to be a constant of the motion for O_2 molecule. The experimental intermolecular dipole–dipole relaxation rate is analyzed using the following equation:[211]

$$\left(\frac{1}{T_1^{DD}}\right)_{\text{inter}} = \left(\frac{1}{T_1^{DD}}\right)_{\text{theor limit}}\cdot F\left(\frac{V}{k_BT}\right)\cdot\left\{1-f(T)\omega^{1/2}\right\} \tag{1.23}$$

where the magnetic field dependence appears as the low-frequency limiting form that applies when the nuclear-spin bearing molecule suffers several

collisions during one Larmor precession of the nucleus, and $F(V/k_B T)$ is a function that is a measure of the collision efficiency that goes to 1 for a hard-sphere spherical potential, that is, the actual effective cross-section is $F(V/k_B T) \cdot \pi d^2$. For ^{19}F in SF_6 in a mixture of SF_6 and O_2, the spin-rotation mechanism, which had been shown to dominate the relaxation rate in pure SF_6, still applies for SF_6–SF_6 collisions, but the intermolecular ^{19}F-electron spin dipole interaction is also operating. Because of the large γ_S, this is a very significant relaxation mechanism. A multiple magnetic field study permits the separation of the field-independent intramolecular $[T_{ISR}]^{-1}$ and the field-dependent $[T_{IDD,inter}]^{-1}$ relaxation rates. The functional form of eqn (1.23) was validated and the temperature dependence of the various parts of eqn (1.23) were found for SF_6 in O_2; further studies were carried out for ^{19}F in CF_4 and SiF_4 in O_2,[212] as well as ^{19}F in SeF_6 and TeF_6 in O_2, and for ^1H in CH_4 in CH_4-O_2 mixtures.[213] By varying the density of O_2 in the samples, it is possible to include a wide range of relative contributions to the relaxation rate. For example, for ^{19}F in CF_4 in O_2, in mixtures such that the relaxation rates are 10%DD/90%SR up to 80%DD/20%SR, we successfully determined the density, temperature, and magnetic field dependence of the intermolecular DD relaxation rate since the dependences of the rates of the two mechanisms on these three factors are opposite, *i.e.*, ρ vs. $1/\rho$, $\sim T^{-1}$ vs. $T^{+3/2}$, 1 vs. $[1 - f(T)\omega_F^{1/2}]$. We find that the experimental $f(T)$ function is reasonably close to our theoretical estimate in eqn (1.24),

$$f(T) = \frac{1}{24} \left(\frac{d}{\bar{v}}\right)^{1/2} \left[3 + 7\left(\frac{\gamma_S}{\gamma_I}\right)^{1/2}\right] \tag{1.24}$$

where the temperature dependence appears only in the $\bar{v}$. At 300 K the theoretical estimate given by eqn (1.24) is between 92% (CF_4 in O_2) and 108% (TeF_6 in O_2) of the experimental values for the six different systems mentioned above.

The temperature-dependent experimental cross-section for intermolecular dipolar interaction with the electron spin of O_2 is $F(V/k_B T) \cdot \pi d^2$. The efficiency $F(V/k_B T)$ is found to increase dramatically in the order $CH_4 < CF_4 < SF_6 < SiF_4 < SeF_6 < TeF_6$ at 300 K,[212] magnitudes that are about 2–4 times as large as for a square well potential counterpart of the best empirical estimates of the PES for the interaction of these molecules with O_2. The temperature dependence of the experimental cross-section is more pronounced than for a square well potential, and likewise becomes more pronounced in the same relative order. It is quite clear that the experimental cross-sections indicate significant long-range contributions.

We also investigated the relaxation of ^{129}Xe in the presence of O_2 gas.[214] In this case the other intermolecular relaxation rates available to ^{129}Xe (such as those described in Section 1.5.7) are much too weak to compete with the relaxation due to ^{129}Xe-electron-spin–dipole interactions during binary collisions when the oxygen densities are significant (mole fraction of O_2 in the Xe–O_2 mixtures > 0.005). The temperature-dependent effective cross-section

$F(V/k_BT) \cdot \pi d^2$ found experimentally is $250(T/300 \text{ K})^{-0.27} \text{ Å}^2$. The relaxation of ^{3}He in the presence of O_2 has been investigated by Saam *et al.*[215] and ^{3}He in the presence of NO by Hayden *et al.*[216] The analysis of the latter is much more complicated in that the effective magnetic moment of the NO is a result of both electron spin and orbital angular momentum that couple and leads to a temperature-dependent effective magnetic moment, in contrast with O_2 in which S is a good quantum number.

1.5.9 Classical Trajectory Calculations of Relaxation Cross-sections

Precise determination of the intermolecular potential energy surface remains one of the most important problems in chemical physics. The accurate and consistent calculation of potential-energy surfaces (PES) for van der Waals complexes, from short through intermediate to large intermolecular separations, remains a severe technical challenge for *ab initio* quantum mechanics. Only a few small systems have been subjected to CCSD(T) level calculations in the limit of complete basis sets. There is thus a need to validate the PES, where possible, against available experimental data, including second interaction virial coefficient, transport properties, and relaxation phenomena data for binary mixtures, crossed-beam total differential and total integral scattering, as well as microwave and infrared spectra for the vdW complex. All these data are required to validate a PES because each is sensitive to a different portion of the PES. For example, the bound state properties associated with microwave and infrared spectra of the vdW complex are fairly well defined for inter-species distances less than 8 Å and the microwave spectrum primarily provides the moment of inertia of the vdW complex, thus the distances and angles close to the global minimum of the PES. The vdW infrared spectra are mainly sensitive to the shape (anharmonicity) of the van der Waals well. Properties such as the virial coefficients and transport and relaxation phenomena require an accurate representation of the long-range part of the PES. Crossed-beam experiments provide a post-collision angular distribution; the dependence of the cross-section on scattering angle is quantified by the differential cross-section. The integral of the differential cross-section (DCS) over scattering angles gives the total or integral cross-section. The supernumerary rainbows arising from interference effects provide information about the range and shape of the potential near the minimum. Total differential and total integral scattering data are therefore sensitive to both the attractive and repulsive parts of the potential, particularly sensitive to the anisotropy (angle-dependence) about the repulsive wall. The NMR relaxation cross-sections $\mathfrak{S}'(0\hat{2}00|A)_{AB}$ and $\mathfrak{S}(0100|A)_{AB}$ are particularly sensitive to the anisotropy of the PES for all intermolecular distances because only anisotropy can cause molecular reorientation or rotational angular momentum change, unlike the interaction virial coefficients that can be accounted for by an isotropic potential, with only minor corrections arising from anisotropy.

A fully classical trajectory code has been developed by Dickinson *et al.* for atom collisions with a diatomic molecule,[217] and for pure gases of linear molecules;[218] finally, the theory has been extended to rigid molecules of arbitrary structure, *i.e.*, asymmetric tops.[219] Since symmetric tops and spherical tops can be considered as special cases of asymmetric tops, this last development allows transport and relaxation properties of important molecules such as benzene, methane, and sulfur hexafluoride to be calculated (but not any molecules that have internal rotation, such as ethane). Given a particular PES function, all the temperature-dependent cross-sections can be calculated using this code, including the cross-sections that are identified with many gas phase thermophysical properties such as binary diffusion coefficients, mixture viscosities, mixture thermal conductivity, mole fraction dependencies of the interaction second virial coefficient, the binary diffusion coefficient, the interaction viscosity, the mixture shear viscosity and thermal conductivity coefficients, field effects on these properties, as well as the cross-sections associated with spin relaxation.

For N_2-Ar, the NMR relaxation cross-sections[182,189] have the tightest experimental uncertainties, and are available over a more extended temperature range than are the effective cross-sections extracted from any other relaxation phenomenon. Among the eight N_2-Ar potential energy surfaces tested by McCourt *et al.*[220] using classical trajectory calculations, one PES, denoted as XC(fit), gives consistently better agreement with the values of $\mathfrak{S}'(0\hat{2}00|A)_{AB}$ determined from the NMR measurements[189] than does any other of the potential-energy surfaces, including the previously "best" MMSV (Morse–Morse–Spline–van der Waals) PES that had been fitted to previously known thermophysical and crossed beam data. The XC(fit) PES does provide distinctly altogether better agreement with these NMR relaxation experimental results than do any of the other four new N_2-Ar potential-energy surfaces the authors considered, and is for the moment the "best" intermolecular potential for N_2-Ar.

We had carried out classical trajectories on six simple model potentials for N_2-Kr;[221] these include a previously published empirical surface derived from fits to molecular beam experiments and various model potentials of the Tang and Toennies type that differ in the set of dispersion coefficients employed. Forty-five effective cross-sections that determine the bulk transport and relaxation phenomena were calculated by classical trajectories for temperatures ranging from 100 to 800 K for each of the six PES. The sensitivity of the NMR-derived cross-sections to the various characteristics of the anisotropy of the potential (such as the anisotropy in the well depth, in the high repulsive wall, in the low repulsive wall, and at $V = 0$) are examined. It is found that both the radial anisotropy and the anisotropy in well depth contribute to $\mathfrak{S}(0100|N_2)_{N2-Kr}$ or σ_J and $\mathfrak{S}'(0\hat{2}00|N_2)_{N2-Kr}$ or $\sigma_{\theta,2}$. The often-assumed empirical power law dependence of the NMR cross-sections on temperature within a 200 degree range (200–400 K) is found to be consistent with the results of the classical trajectory calculations of these cross-sections for all of the six potentials considered, although a more complex

temperature dependence would be necessary to describe a much greater temperature range. It was found that better overall agreement with experimental data previously considered could be obtained by slight modification of one of the previously used potentials.[222] A modification of this surface to include a recent *ab initio* determination of the C_6 dispersion coefficient, and to bring in the virial and microwave data, gives a new potential surface that is in good agreement with all available experimental data and thus could be considered as the current best N_2-Kr PES.

We subsequently carried out a similar study of the CO_2–Ar potential.[223] Twelve potential energy surfaces that have been proposed for the CO_2–Ar interaction were considered in detail. The anisotropies of these surfaces are compared and their ability to predict the interaction second virial coefficient as a function of temperature has been examined. Intermolecular bending and stretching quadratic force constants predicted by each and the mean square torque calculated for each are compared with the experimental values. Quantum diffusion Monte Carlo simulations provide the average rotational constants and geometry for the ground vibrational state as well as the dissociation energy in each case. These are compared with the experimental values. Classical trajectory calculations were carried out to obtain 45 types of thermal average cross-sections for six of these surfaces. Various thermophysical properties calculated from these cross-sections and the NMR relaxation cross-sections are compared with experimental data. It is found that the spectroscopic constants define the depth and shape of the well at the global minimum, whereas the NMR cross-sections and mean square torque probe the anisotropy in a broader sense. The thermophysical properties (viscosity, diffusion coefficient, and thermal conductivity) are not strongly discriminating between the surfaces, whereas the temperature dependence of the second virial coefficient detects the weaknesses in the low and upper repulsive walls of those surfaces that were modified specifically to improve greatly the shape of the well so as to reproduce the spectroscopic constants.[223] A more recent *ab initio* PES for CO_2–Ar has been calculated and tested only against the infrared spectra of the vdW complex.[224] It remains to be seen whether this one can reproduce the NMR relaxation data and the thermophysical properties. We also carried out trajectory calculations for NNO-Kr and NNO-Ar.[225] The available PES are unable to reproduce both NMR cross-sections accurately. Similar studies have been carried out by Dickinson *et al.* for N_2–N_2 and CO_2–CO_2, using the NMR relaxation cross-sections and thermophysical properties in a multi-property analysis of the PES.[226,227]

1.5.10 The Special Case of Hydrogen Molecule

Some of the earliest theoretical treatment and experimental T_1 studies in the gas phase involved the hydrogen molecule.[228,229] Experimental studies of H_2, HD, and D_2 in collisions with rare gas atoms were carried out by Armstrong, McCourt, and co-workers in He and Ne,[230–233] and by McCourt *et al.* in

Ar.[234–237] These experiments were accompanied by theoretical calculations that permitted the testing of various *ab initio* and semi-empirical potential surfaces for H_2, HD, or D_2 interacting with He, Ne, or Ar. A study of the relaxation times of all the isotopomers of hydrogen in Ar gas have been carried out by McCourt *et al.* over the entire density range from the reciprocal density regime through the T_1 minimum all the way to the linear-density regime,[236,237] and then they carried out a full critical test of a new PES for this system.[235] For hydrogen molecule, a classical treatment does not apply because the rotational energy levels are very widely spaced, so only a quantum-mechanical approach can be used. They used a potential function that Bissonnette *et al.* determined by modifying a starting exchange-Coulomb type PES fitted to highly accurate spectroscopic data for H_2-Ar, D_2-Ar, and HD-Ar van der Waals molecules, plus interaction second virial coefficient data and Raman collisional shift data for H_2–Ar binary mixtures.[238] Utilization of this particular set of data ensures that both the isotropic component of the PES and the anisotropy in the potential well are determined very accurately. Indeed, this PES provides excellent agreement with bulk transport and relaxation data not utilized in the determination of the original PES. Using quantum-mechanical close-coupled computations based on the H_2–Ar potential energy surface obtained by Bissonnette *et al.* and using all the ^1H and ^2H relaxation data, McCourt *et al.* concluded that significant differences found between the experimental and theoretical results indicate that the short-range anisotropy of the proposed PES is too weak. The reciprocal density regime (densities below the T_1 minimum) is shown to have a much higher sensitivity to changes in the anisotropic component of the intermolecular potential energy surface than the linear-density regime, and therefore, for H_2–Ar, the discrepancy between the calculated and experimental cross-sections is a much more stringent test of the PES.

1.6   Conformational Dynamics in the Gas Phase

N. S. True and co-workers have developed the use of pressure-dependent gas phase NMR spectroscopy as a probe of conformational dynamics in the gas phase. Their present capabilities allow spectral acquisition at sample pressures as low as 0.1 torr. With these capabilities they are able to pursue studies that address both the accumulation and the disposal of intra-molecular and intermolecular vibrational energy in simple molecules undergoing structural exchange. Gas phase NMR studies have also been carried out on several other systems such as PF_5, ethers and alkyl nitrites, and cyclic amines. Since, for many of these systems, it is possible to obtain rate data in the bimolecular kinetic region, they can probe intermolecular energy transfer efficiencies accompanying these processes. They also can determine temperature-dependent equilibrium constants, and activation thermodynamic quantities for chemical exchange processes, that can provide stringent tests of high-level *ab initio* calculations of transition states and

activation energies. Temperature-dependent equilibrium constants for conformational equilibria that have been measured by the True group in the gas phase include the keto ↔ enol tautomerism of acetyl acetone,[239] the syn ↔ anti conformational equilibrium of methyl nitrite,[240] and the larger nitrites *n*-propyl, *n*-butyl, and isobutyl nitrite.[241,242]

The rate constants for chemical exchange processes in the gas phase are pressure-dependent due to competition between bimolecular deactivation and reaction of energized molecules. Three pressure regions can in principle be observed for a gas phase chemical exchange process, namely unimolecular at high pressure, fall-off at intermediate pressure, and bimolecular at low pressure. Internal rotation has been studied for several symmetrically substituted amides at or near the unimolecular limit,[243–246] and also for thioamides.[247] In each case, exchange-broadened ^{1}H spectra were obtained for samples containing the amide at its vapor pressure and several atmospheres of an inert gas; measurements were made at several pressures to ensure that the rate constants were at the unimolecular limit. ^{13}C spectra in isotopically enriched samples have also been used, for example, to measure the rate constants in *N,N*-dimethylformamide.[248] Gibbs activation energies are 5–10 kJ mol^{-1} lower in the gas phase than those in solution. Activation energies for ring inversions in various molecules have been studied, for example cyclohexane,[249] cyclohexene,[250] tetrahydropyran,[251] *N,N*-dimethylpiperazine,[252] *N*-methylpiperazine,[253] *N*-methylpiperidine,[254] and *N*-ethylmorpholine.[255] The degenerate Cope rearrangement of bullvalene [tricyclo(3.3.2.0)deca-2,7,9-triene] was observed in ^{1}H NMR in the gas phase in samples with 1 torr of bullvalene in a 6 up to 2580 torr of a bath gas (SF$_6$).[256] The measured pressure-dependence of the rate constants at 356 K are in the unimolecular and fall-off kinetic regions. For the bullvalene rearrangement the bimolecular kinetic region occurs at pressures considerably below 5 torr. Unimolecular rate constants obtained for the rearrangement are *ca*. 15% lower than those observed in solutions of bullvalene in CS$_2$(liq) at the same temperatures.

Data on pressure-dependent rate constants of unimolecular processes provide tests of statistical kinetic theories such as RRKM (Rice–Ramsperger–Kassel–Marcus).[257,258] RRKM theory is the method of choice for practical predictions of gas phase dissociation and isomerization rate coefficients. Account is taken of the way in which the different normal-mode vibrations and rotations contribute to reaction, and allowance is made for the zeropoint energies. The total internal energy is partitioned into active and inactive components, such that only the active component can flow freely among the internal modes and thus contribute to reaction. The assumed equilibrium ratio of active-to-inactive components is evaluated using partition functions. In applications where gas-phase collisions are important, the rates of activation and deactivation take into account their energy dependence, and in the high-pressure limit the transition state is in equilibrium with non-activated reactants and RRKM reduces to conventional transition-state theory. RRKM and other statistical kinetic theories assume

that the rate constant for intramolecular energy redistribution in critically energized molecules is rapid (compared with the energy-dependent rate constant) and ergodic. Statistical theories of chemical reactions are therefore most applicable to large molecules undergoing processes at high activation energies. However, at the low activation energies required for conformational processes, critically energized molecules have sparse density of states and the anharmonic coupling constants among vibrational states are small. Under these conditions, statistical kinetic theories may not provide an adequate description of these processes. Conformational processes of the small molecules studied in the gas phase by the True group are just the type of systems that may challenge the assumptions of RRKM theory.

When the process can be modeled with RRKM theory, it is valid to apply transition state theory to the high-pressure rate constants. When this is the case, then accurate *ab initio* calculations of ground- and transition-state structures and vibrational frequencies can be used to predict gas-phase activation parameters (ΔG^+_{298}, ΔH^+_{298}, ΔS^+_{298}) for internal rotation (or pseudorotation or ring inversion) that can then be directly compared to the corresponding activation parameters that are experimentally obtained from the temperature-dependent kinetic data from ^{1}H (or ^{13}C or ^{19}F) NMR in the gas phase. Note that all this is possible only for dilute gas phase results, but not for solution phase data. Only data obtained in the dilute gas phase can be used to test quantum calculations of ground state structures, transition state structures, vibrational frequencies, and activation barriers since in these solvent-free systems it is actually possible to use the highest levels of quantum-mechanical theory and not to have to resort to DFT or MD simulations with empirical force fields that are the typical theoretical approaches to condensed phase kinetics. We illustrate with two examples from work in the dilute gas phase by True *et al*.

The True group has carried out ^{1}H experiments to observe the chemical exchange spectra for 2 torr of ^{15}N-trifluoroacetamide in 600 torr of bath gas (SF$_6$) and for 1 torr of the molecule in 300 torr of the SF$_6$.[259] They had previously shown that the internal rotation process for this molecule was statistical. From the total line shape analysis they obtained the activation parameters for internal rotation of trifluoroacetamide. Their *ab initio* MP2 calculations of these activation parameters agree with experiment within experimental errors, whereas DFT calculations (with the B3PW91 functional) using the same basis set did not.

Another example is the Berry pseudorotation in SF$_4$, which concertedly exchanges the magnetically inequivalent sets of axial and equatorial F atoms. This is one of the smallest molecules that undergo an intramolecular rearrangement that has rate constants accessible to NMR measurement.[260] The True group found that the strong collision RRKM model as applied to Berry pseudorotation of SF$_4$ reproduces very well their experimental pressure-dependent rate constants at 335 K. The curvature and displacement of the experimental fall-off curve are not significantly perturbed by effects of

weak collisions and non-statistical intramolecular vibrational energy re-distribution. Since the process can be modeled with RRKM theory, it is valid to apply transition state theory to the high-pressure (at 7.9 atm) rate constants. From analysis of the exchange-broadened ^{19}F NMR spectra, they obtain the temperature-dependent rate constants characterized by $E^{\infty} = 11.9(0.2)$ kcal mol^{-1}, $A^{\infty} = 3.56(1.09) \times 10^{12}$ s^{-1}, and the activation parameters $\Delta G^{\ddagger}_{298} = 12.2(0.1)$ kcal mol^{-1}, $\Delta H^{\ddagger}_{298} = 11.3(0.4)$ kcal mol^{-1}, and $\Delta S^{\ddagger}_{298} = -3.3(0.4)$ cal mol^{-1} K^{-1}. Quantum calculations at the MP4 level predict $\Delta H^{\ddagger}_{298} = 11.55$ kcal mol^{-1} and $\Delta S^{\ddagger}_{298} = -3.91$ cal mol^{-1} K^{-1}, in excellent agreement with their experiment, whereas DFT calculations (using hybrid functionals B3LYP and B3PW91) provide considerably less accurate results.

Reviews of the experimental and theoretical work in these areas provide an overview.[6,7]

List of Abbreviations

CASSCF	Complete active space self-consistent-field method
CCSD	Coupled-cluster singles and doubles method
CCSD(T)	CCSD model augmented by perturbative corrections for triple excitations
CSA	Chemical shift anisotropy
DCS	Differential cross-section
DD	Dipole–dipole
DFT	Density functional theory
efg	Electric field gradient
FC	Fermi contact
FCI	Full configuration interaction
MCSCF	Multi-configuration self-consistent-field method
MD	Molecular dynamics
MMSV	Morse–Morse–Spline–van der Waals potential function
MP2, MP3, MP4	Møller–Plesset perturbation theory (second, third, fourth order)
NMR	Nuclear magnetic resonance
PES	Potential energy surface
RASSCF	Restricted active space self-consistent-field method
RHF	Restricted Hartree–Fock
SO	Spin–orbit
SOPPA	Second-order polarization propagator approximation
SR	Spin-rotation
UV	Ultraviolet
vdW	van der Waals
ZPV	Zero-point vibration

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