Magnetic Deflection Spectrum of VCl₄

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Abstract: The magnetic deflection spectra of VCl₄ seeded into supersonic beams of the rare gases have been determined. It is found that in the heavier rare gases (Ar, Kr, and Xe) the Stern–Gerlach splitting patterns are just those expected for a molecule in a spin-doublet state, as complicated by the presence of nondeflecting (VCl₄)ₓ clusters. In these beams, the satellite splittings of unclustered VCl₄ scale with the square of the beam velocities, and there is no evidence in the Stern–Gerlach spectra for the rapid (10^{-9} s) intramolecular spin relaxation (ISR) so apparent in the EPR and NMR spectra of this molecule in condensed phases. Modeling of the ISR effect on SG deflection spectra and comparison of these results with experiment shows that if ISR is in any way active in beam-cooled VCl₄, the spin relaxation time is longer than 10^{-4} s. By contrast, the deflection spectrum of VCl₄ seeded into He is far more compressed than otherwise expected, suggesting that ISR may be at work in this case. Analysis of the observed Stern–Gerlach band shape of VCl₄ in the He beam shows that if ISR is the cause of the anomalous spectrum, then the ISR time is approximately 10^{-6} s. The use of magnetic deflection to determine the possible association of the carrier gases with the paramagnetic target molecule is presented as an illustration of neutral-molecule mass spectrometry.

We have been involved recently in studying the interactions of magnetic molecules with inhomogeneous magnetic fields using the Stern–Gerlach deflection technique. In this method, the magnetic molecule, used either pure or seeded into a rare gas, issues from a pulsed valve/dual skimmer arrangement to form a well-collimated supersonic molecular beam passing between the poles of a gradient magnet. Depending upon the magnetic substate M_j of the molecule, it may be deflected by the field gradient into the region of higher field, into the region of lower field, or not at all. The spatial dispersion of the beam is measured by tuning a mass spectrometer to the mass of the magnetic species of interest while translating the spectrometer in each case in a direction normal to that in which the beam is traveling but parallel to the direction of the field gradient. Working in this way, we have studied the magnetic deflection spectra of oxygen and its clusters[1] and of nitrogen dioxide, nitrous oxide, and some organic nitroxide radicals.[2]

The deflection of the molecular beam by the magnetic field gradient is in response to the force resulting from the coupling of the field gradient to the net molecular angular momentum projected onto the direction of the field gradient, M_j. This net angular momentum (J before projection) in turn results from the internal coupling of angular momenta arising from various sources of periodic angular motion within the molecule. The internal momenta generally can be associated with either electron motions (uncompensated electron spin and/or uncompensated degenerate orbital motions) or nuclear motions (nuclear spin, internal vibrations of high degeneracy, and/or end-over-end tumbling of the molecule, which populates rotational levels having rotational quantum number $N > 0$). Though the electron motions by themselves generally result in much larger couplings to the field gradient than do the nuclear motions by themselves, because of the coupling of the electron motions to the nuclear motions (as by the spin-rotation interaction, for example), the latter cannot be ignored generally in the presence of the former. In all of our work to date, the deflected molecule had electronic angular momentum due to the presence of one or more unpaired electron spins in addition to angular momentum arising from one or more of the other sources.

Implicit in the magnetic deflection experiment is the assumption that the orientation of the net angular momentum projection M_j during the flight of the molecule through the deflecting magnet

gap is not relaxed by any means as, for example, by electron spin relaxation. This may not always be the case, however, for Amirav and Navon[3,4] have reported apparently anomalous behavior when working with the magnetic deflection of paramagnetic heavy-metal complexes seeded into molecular beams. Noting that in certain such systems the paramagnetic molecules (chromium acetylacetonate and UBr₄, for example) appear not to be deflected, Amirav and Navon have attributed this as due to an intramolecular spin relaxation (ISR), leading to lifetimes (τ) in the nanosecond to microsecond range. That is to say, the electron spins in those paramagnetic compounds with τ in the nanosecond to microsecond range undergo many flips within the magnet gap. Were the molecule a spin-doublet, the force on it within the magnet gap would reverse direction with each spin flip, with the net effect on the deflection spectrum depending upon how τ compares with t, the residence time of the molecule in the field gradient. With τ very short compared to t, one might expect that the effect of ISR would be to slightly broaden the line profile beyond that observed at zero field as the ISR acts against the tendency of the line to split into spatially resolvable $M_J = +^1/_2$ and $M_J = -^1/_2$ components at high fields. On the other hand, if τ is very long compared to t, then the ISR would be expected to have no effect on the SG spectrum. According to Amirav and Navon, the ISR mechanism is intimately related to the strong spin-orbit coupling induced by the central metal atom.

In this paper, we present magnetic deflection results for the transition-metal compound vanadium tetrachloride, along with theoretical predictions as to what the effects of ISR on the Stern–Gerlach band shapes for such a molecule would be if such a relaxation were to occur. As is well-known, VCl₄ has a nominally tetrahedral geometry and contains a single unpaired electron in a 3d orbital of E symmetry.[5–7] As pointed out by Parameswaran et al.,[8] an electron in the E orbital of VCl₄ has zero orbital angular momentum, and so spin–orbit coupling is of no direct consequence in the ground state. On the other hand, the ²E ground state of VCl₄ is theoretically susceptible to both static and dynamic Jahn–Teller distortions. Experimental[8–10] and theoretical[11–15]

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studies of the problem of Jahn–Teller instability in VCl_4 lead to the conclusion that there is no large static distortion in this molecule but that there is a dynamic distortion involving the ν_2 vibrational coordinate of E symmetry and a 3-fold potential barrier. In the vicinity of room temperature the distortion is essentially dynamic, however, at very low temperatures the 3-fold barrier might act to trap the molecule in a slight static distortion. The barrier height is calculated to be between 10 and 200 cm^{-1}.

With respect to the question of the importance of ISR processes to the observation of a finite magnetic deflection in transition-metal complexes,[2-4] it is most interesting to note that studies of the electron spin[9,15,16] and NMR[17] spectra of VCl_4 in condensed phases indicate that τ for the unpaired electron is less than 1 ns. Johannesen et al.[9] suggest that the very short τ of VCl_4 is due to spin flips induced by the rapid transitions between the minima of the 3-fold Jahn–Teller potential. Only at temperatures in the vicinity of the boiling point of liquid He does the τ of VCl_4 lengthen sufficiently to allow ESR signals to be observed.[9]

Were the spin-flip mechanism of Johannesen et al. operating for VCl_4 in a molecular beam, then the molecule would undergo ca. 10^5 spin flips in the course of traversing the magnet, and consequently the magnetic deflection spectrum of this species would be expected to show no M_J splitting, though a slight broadening of the undeflected peak possibly might be seen upon energizing the magnet. On the other hand, if the vibrational temperature of the molecules in the beam were low enough, they would be trapped in static distortions by the 3-fold barriers and thus τ would be lengthened considerably. As τ lengthens and so approaches the transit time of the molecule through the magnet gap (ca. 10^{-4} s), the deflection forces become more sustained and a splitting pattern can develop. That temperatures low enough to trap VCl_4 in one of its Jahn–Teller minima might be a factor in the beam studies is indicated by the fact that rotational and translational temperatures of 2–10 K are routinely achieved in supersonic expansions such as were used here.[18] On the other hand, there is no guarantee that the vibrational temperature is this low; it is also possible that the rapid spin flip in VCl_4 requires a surrounding medium for reasons of energy and angular momentum conservation and thus is irrelevant when the molecule is isolated in a molecular beam.

In order to assess the possibility of ISR distortion of the magnetic deflection pattern of VCl_4, we have made a detailed theoretical study of how ISR can affect the Stern–Gerlach band shapes.[19] Without going into the details of the calculation, we present here some of the results of this work as they apply to the question of the effect of ISR on the deflection spectrum of VCl_4.

Regardless of the spin-flip complication, our expectation is that any V or Cl nuclear moments will not affect the deflection spectrum of VCl_4 at our resolution and that the only other possible sources of angular momentum will be the electron spin and the molecular rotation; excitation of the low-lying (135 cm^{-1}) ν_4 deformation of t_2 symmetry[7] does impart angular momentum to the molecule; however, it will be of little consequence if in fact the vibrational temperature is already so low as to freeze the molecule into one of its static Jahn–Teller configurations. That the vibrational cooling in ν_4 will be substantial is guaranteed by its very low frequency. If the electron spin is the only source of angular momentum in cold VCl_4 and the ISR mechanism is not func-
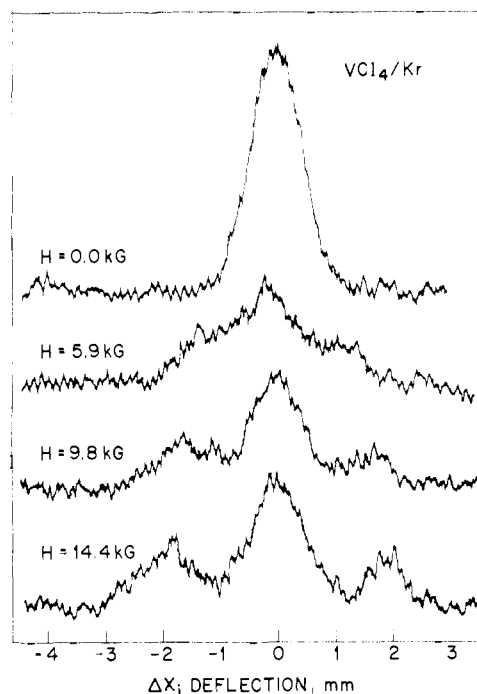

Figure 1. Magnetic deflection spectra of VCl_4 (1.9 Torr) seeded into Kr (50 Torr), as a function of magnetic field gradient. Spectra were recorded by monitoring the VCl_4^+ parent ion.

tioning, the splitting pattern will consist simply of two symmetry displaced satellites ($M_J = +^1/_2$; $M_J = -^1/_2$), having equal intensity, and each with a width equal to that of the undeflected beam at zero field.

We have determined the magnetic deflection spectrum of VCl_4 using the apparatus previously described.[1] The commercial material was freed of HCl and Cl_2 by pumping the cooled sample until the vapor pressure reached that reported for the pure liquid. Aliquots of the vapor were then mixed with the various rare gases, and the gas mixtures were used to pressurize a stainless steel pulsed valve having a nozzle diameter of 0.05 cm. The spatial profile of the deflected beam was determined using a translatable mass spectrometer mounted behind an 0.025-cm slit and tuned to the parent ion VCl_4^+. The reason for using the various rare gases from He to Xe as carriers for the VCl_4 is that each has a different residence time within the magnet and each cools the VCl_4 to a different degree, with Xe having the largest rotational and vibrational cooling effect and the longest residence time and He the smallest cooling effect and the shortest residence time for a given stagnation pressure.

In this work, it was found that at high rare-gas backing pressures, large signals of VCl_4^+ were seen; however, there was no spatial deflection of the beam species when the magnet was energized. Reduction of the rare-gas backing pressure to the lowest possible value while still retaining some VCl_4 signal yielded deflection spectra showing more or less of the undeflected peak together with satellite peaks. Just this type of behavior was observed earlier in the case of the magnetic deflection spectrum of NO_2 seeded into rare gases[2] and was interpreted in the following way. At high backing pressures of the rare gases, the cooling upon expansion to form the beam leads to the formation of diamagnetic or weakly paramagnetic clusters, which are magnetically undeflected but which fragment in the ionizer to parent ion. At lower backing pressure where the cooling is not as severe, the clustering is incomplete and so the spectrum also contains satellite peaks due to the monomer. In the cases of both NO_2 and VCl_4, the appearance of the monomer deflections requires a lower backing pressure, the heavier the carrier gas.

The magnetic deflection spectra of VCl_4 (1.9 Torr) seeded into Kr carrier gas (50 Torr) at various values of the applied magnetic field (as measured at the approximate center of the "sweet zone"[1] are shown in Figure 1. With increasing field, the undeflected

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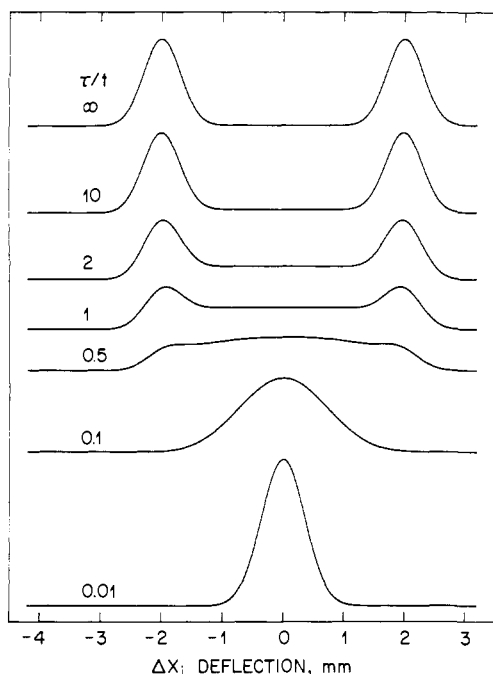
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Figure 2. Magnetic deflection profile computed for an unspecified spin-doublet molecule in a constant magnetic field gradient as a function of $\tau/t = \lambda$.[19] A more detailed view appears in Figure 3.

Figure 3. Detailed view of the behavior of one of the spin-doublet satellite peaks computed as a function of $\lambda = \tau/t$.

peak is seen to diminish while at the same time, two satellite peaks appear with symmetrical displacements about the central peak. Our interpretation here is that the two satellite peaks are just those expected for VCl_4 behaving as a spin-doublet molecule; as such, the pattern closely resembles that observed for NO_2 ($^2A_1$), for example.[2] However, as was also the case with NO_2, the expansion of the VCl_4/Kr mixture also results in a certain amount of clustering of the seed molecules. Indeed, the parameter-controlling clustering is $p_0^2 d$ where p_0 is the stagnation pressure and d is the nozzle diameter; in the present case $p_0^2 d$ equals 125 Torr^2 cm, which is quite large enough to promote formation of $(VCl_4)_x$ clustering in the Kr beam.[18] To the extent that the heavy $(VCl_4)_x$ clusters are diamagnetic or weakly paramagnetic (but not ferromagnetic) and dissociate in the ionizer of the mass spectrometer to yield the parent ion VCl_4^+, a peak will then appear at or near zero deflection, as observed in Figure 1. The fact that essentially the same deflection pattern is observed when the Kr partial pressure is dropped from 50 Torr (Figure 1) to as low as 19 Torr implies that the value of $p_0^2 d$ (20 Torr^2 cm) at 19 Torr Kr apparently is still within the clustering regime, for the intense central peak remains in the deflection pattern. Reasons for discounting the central peak as due to small clusters of $VCl_4 \cdot Kr_x$ are given below.

That no further structure beyond the three-line pattern is apparent in the spectra of Figure 1 implies that either the sample is so cold that only $N = 0$ rotational levels are occupied or that if higher N levels are populated, the spin–rotation coupling is weak and so is readily broken by external fields of ca. 10 kG or less (the Paschen–Back effect).[1] The latter is seen to be plausible by the following argument. The field at which Paschen–Back uncoupling becomes effective depends upon both the spin–rotation coupling constant ϵ and the spin–spin coupling constant λ.[19] For spin–triplet molecules such as O_2, it is λ that dominates and leads to Paschen–Back effects at fields above ca. 10 kG. In contrast, in a spin-doublet molecule such as NO_2 where λ is necessarily zero, only ϵ is effective in spin–rotation coupling and so Paschen–Back effects commence at fields as low as 0.1 kG.[2] VCl_4, being a spin doublet, has $\lambda = 0$ and so is expected to show Paschen–Back uncoupling at very low fields, as in NO_2.

In order to aid in the interpretation of the magnetic deflection spectra of VCl_4, we have calculated how an increasingly rapid ISR would affect the band shapes of a molecule such as this were it operative.[20] We have solved exactly the random walk model for
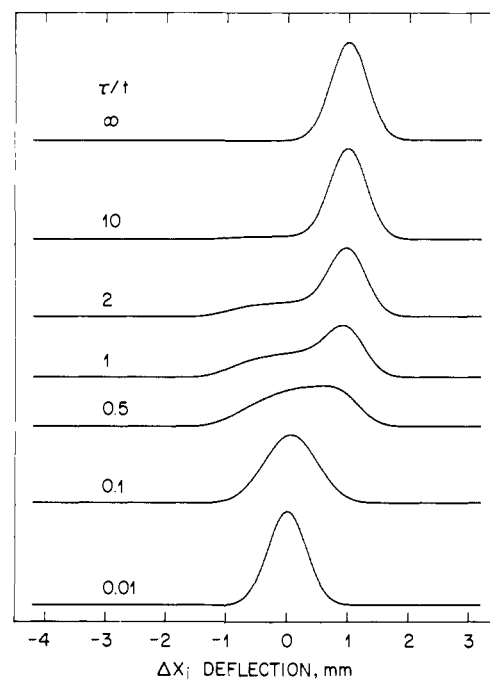
spin flips in a magnetic field as a function of the dimensionless parameter $\lambda = \tau/t$, where τ is the electron spin relaxation time for exponential decay of the spin alignment and t is the residence time of the spin-doublet molecule in the magnetic field gradient (ca. 10^{-4} s).[21] As shown in Figure 2, when λ is larger than ca. 10, it is calculated that there will be no noticeable effect on either the satellite positions or their widths. When λ is in the range between 10 and 1, the satellite peaks move toward one another slightly while broadening with extreme asymmetry toward the position of zero deflection. This asymmetry is shown in more detail in Figure 3. When λ is between 1 and 0.5, the asymmetric coalescence continues such that the two individual peaks due to $M_j = \pm^1/_2$ spin orientations are no longer recognizable at the lower value, having been replaced by a very broad and irregular feature centered at zero deflection. With λ smaller still, only a single symmetric peak remains; it is centered at zero deflection and has a width that is approximately double that of the zero-field line when $\lambda = 0.1$ and that is essentially equal to that of the zero-field line when λ becomes as small as 0.01.

Earlier work[1,2] shows that the somewhat larger width of the VCl_4 satellite at negative deflection (Figure 1) is artifactual, being due to the pecularities of our magnetic field gradient.[22] It is interesting to note that after correction for this inhomogeneity in the gradient, the half-widths of the VCl_4/Kr central and satellite peaks are no larger than that of the peak at zero field. As seen from Figure 2, this constancy of width implies that $\lambda > 1$, from which we deduce that τ is greater than 10^{-4} s in the Kr beam whereas τ is less than 10^{-9} s in the condensed phase. That is to say, unlike the situation in the condensed phase, there are no significant spin-flip transitions occurring within the magnet gap that would otherwise act to diffuse the VCl_4 beam spatially. The relatively large value of τ in the gas phase may be interpreted to mean either that the ISR mechanism simply is not operative in the gas phase or that the cooling of the VCl_4 in the expansion is so strong that the molecules are firmly trapped in the Jahn–Teller minima and so cannot promote spin flips by undergoing thermally

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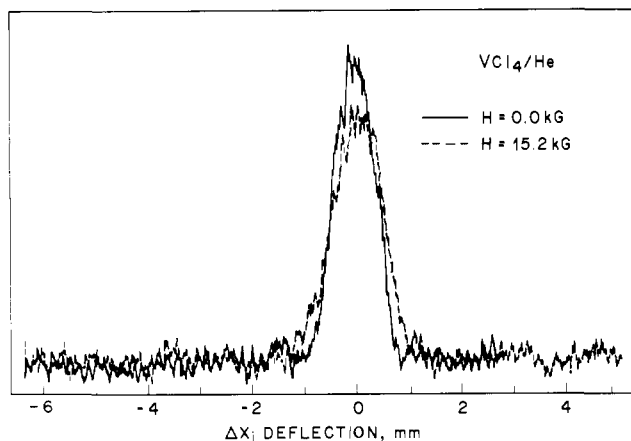
Figure 4. Magnetic deflection spectra of VCl_4 (3 Torr) seeded into He (17 Torr), at two values of the magnetic field gradient. Spectra were recorded by monitoring the VCl_4^+ parent ion.

assisted transitions between minima.

The magnetic deflection spectra of VCl_4 seeded into the other rare gases also were determined. In the case of He as carrier gas, a wide variety of partial pressures of both components could be investigated; however, only the slightest hint of a magnetically induced splitting could be seen in the beam profiles, even at the lowest He pressures and highest magnet currents, Figure 4.

An unavoidable factor operating here is that of the velocity of the molecular beam. The higher the beam velocity, the shorter the molecule's transit time through the magnet, the shorter the time the gradient acts upon the projection of the net angular momentum, and the smaller the deflection; for this reason the magnetic deflection is predicted to vary inversely with the square of the beam velocity. The high velocity of the He beam (7.5 × 10^4 cm/s at a stagnation pressure of 17 Torr, as measured by leading-edge time of flight) thus acts to limit the deflection a VCl_4 molecule will experience while in the magnet gap. Just such a velocity-related lack of splitting was observed when studying the deflection spectra of the nitroxide radical TEMPO seeded into He gas[2] and of the Al atom and the Al_3 cluster also seeded into He;[23] on the other hand, satellite deflection peaks of these paramagnetic species were readily observed when they were seeded into the slower moving Ar. In the case of VCl_4 seeded into the rare gases, the observed velocities in Kr and He and the splitting observed in Kr can be used to predict that the satellites in He will be displaced from the central line by ±0.55 mm at 14.4 kG. As our instrument will readily resolve satellites separated by such a distance from the central peak, the observation (Figure 4) of only a slight broadening of the central peak suggests that if our calculation of the velocity effect is correct, another factor beyond the velocity is limiting the spatial deflection of the VCl_4 when seeded into He.

The lack of observable splitting in the VCl_4/He beam is qualitatively consistent with the idea that the VCl_4 in this case is totally clustered as $(VCl_4)_x$, which is either diamagnetic or only weakly paramagnetic. However, our experience has been that He is the warmest of the rare-gas carriers in spite of its low translational temperature and so offers the least possibility for clustering. Indeed, the p_0^2d factor of ca. 100 Torr² cm appropriate to the spectra of Figure 4 is far below the value of 50 000 Torr² cm above which clustering commences in He beams.[16] Thus it is concluded that the lack of observable splitting in VCl_4/He cannot be explained completely as due either to the high velocity of the carrier gas or to clustering.

By default, one is led to suspect that an ISR mechanism might be at work in the case of VCl_4 seeded into He. In the context of the ISR mechanism of Johannesen et al., one argues that, in the case of He as carrier gas, the vibrational cooling is insufficient to quench the transitions between the Jahn–Teller minima and
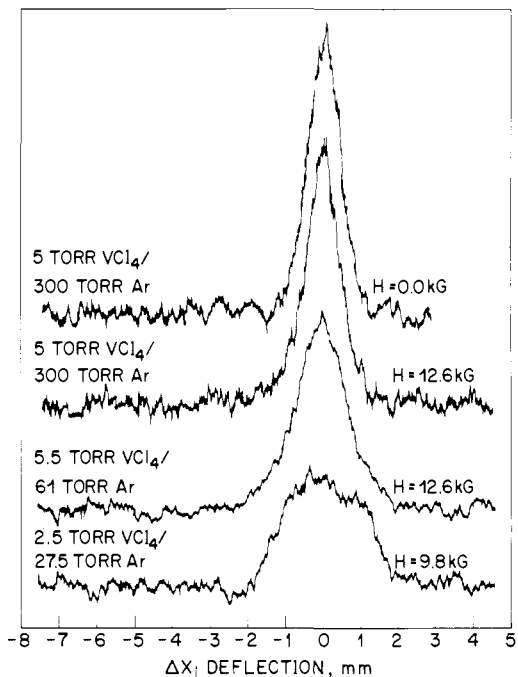
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Figure 5. Magnetic deflection spectra of VCl_4 seeded into Ar as a function of magnetic field gradient and partial pressures of carrier gas and seed. Spectra were recorded by monitoring the VCl_4^+ parent ion.

that the spin orientations are therefore fluctuating so fast as to inhibit the magnetic splitting. Indeed, as can be seen qualitatively from Figure 2, the incipient broadening of the spectrum shown in Figure 4 is consistent with τ, in this case being ca. 10^{-6} s. The short τ and the assumed hopping among Jahn–Teller minima implies a rather high temperature for the VCl_4 in the beam (>10 K) whereas one calculates that the translational temperature of the VCl_4/He beam is only 0.7 K; if the other modes are in thermal equilibrium with the translational mode, then hopping between the Jahn–Teller minima would be frozen out at this temperature. However, experience shows that, for molecules seeded into He, the temperature of the internal modes is far above that of the translational mode,[18] and so the ISR mechanism remains a possibility. In contrast, the internal-mode and translational temperatures of molecules seeded into the heavier rare gases are much more nearly equal. We note too that the quantitative ISR theory of ref 20 is not strictly applicable to the case of VCl_4/He, for the theory assumes the same τ for all vibrational levels, whereas the core of our hypothesis is that τ might be level-dependent in VCl_4.

The possible effects of velocity and ISR on the deflection pattrn of VCl_4/He can be easily distinguished by using a longer magnet. In the case of the velocity effect, the longer magnet will act to further resolve the component satellite peaks, whereas if ISR is operative, the use of a longer magnet will lead to a further broadening, but will not serve to further resolve the broadening into distinct peaks. The effect of using a longer magnet on the VCl_4/He splitting pattern is now being investigated.

When Ar is used as the carrier gas, results intermediate to those for He and Kr are obtained, i.e., application of the magnetic field produces severe broadening of the central peak but not sufficiently as to yield distinct, well-resolved satellite bands (Figure 5). Again, our explanation is that the Ar carrier has an intermediate velocity and so the VCl_4 when seeded into Ar displays an intermediate splitting. In support of this, the measured velocity of the Ar beam (5.8 × 10^4 cm/s at a stagnation pressure of 27.5 Torr) when compared to that of the Kr beam leads to predicted displacements of ±0.90 mm at 9.8 kG for each of the VCl_4 satellites in the VCl_4/Ar beam, and indeed, the satellite shoulders are centered at ±0.96 mm at this field (Figure 5). This figure illustrates as well how the use of high backing pressure results in nondeflective $(VCl_4)_x$ clusters whereas lower pressures of the same backing gas results in satellite features characteristic of monomeric VCl_4.

Unlike the situation when He is used as carrier gas, the translational and rotational temperatures are in equilibrium when using Ar. Thus in the case where 50 Torr of Ar is used as carrier, the translational and rotational temperatures are calculated to be 4.5 K and a relatively intense peak at $\Delta X_i = 0$ due to $(VCl_4)_x$ clusters is observed (figure 5). As the rotational temperature of the VCl_4 in the experiment involvi ig 27.5 Torr of Ar is only marginally within the regime in which the Jahn-Teller motions may be frozen out and the vibrational temperature certainly will be higher still, the satellite structure observed at the expected positions in the splitting pattern (Figure 5) argue against a rapid ISR mechanism, which predicts broadening but not splitting in warm VCl_4.

Finally, experiments carried out with Xe as carrier gave spectra much like those obtained with Kr, but with smaller signal-to-noise ratio. Satellite structure however was readily seen, in this case with a splitting larger than that observed in Kr, due to the lower velocity of the Xe beam (3.75×10^4 cm/s). This velocity leads to the expectation of satellites at ± 2.32 mm at a field of 14.4 kG, while the observed displacement is ± 2.65 mm.

The good agreement between the observed satellite spacings of VCl_4 seeded into the different rare gases and the splittings calculated on the basis of the measured velocities is possible only if the mass of the deflected species is constant in the series of experiments. Thus it is concluded that the deflected species in our beams are in no way complexed with the carrier gases. This principle of neutral-molecule mass spectrometry is useful also in identifying the species responsible for the central peak in Figure 1. Thus the possibility that the central peak is due to the mixed cluster $VCl_4 \cdot Kr$ is readily discounted, for this species is expected to have a deflection of ± 1.34 mm provided that the cluster is beyond the Paschen–Back limit so that coupling of S to rotations is irrelevant. If it is assumed that the central peak instead consists of two overlapping components with deflections of less than ± 0.1 mm and that the species responsible for these peaks is the mixed cluster $VCl_4 \cdot Kr_x$, then the small deflection amplitudes lead to $x \simeq 40$ or larger.

Interpretation of the Stern–Gerlach deflection spectra of VCl_4 seeded into the heavier rare gases is reasonable assuming that the ISR processes are not important in these beams and that the spectral patterns are dictated by the coupling of a single electron spin to the external field, as influenced by beam velocity effects and by clustering to form $(VCl_4)_x$. ISR processes are insignificant here either because they do not occur in the free VCl_4 molecule or because the Jahn–Teller motions provoking ISR are frozen out in the Ar, Kr, and Xe beams. However, in the case of He as carrier gas, it is conceivable that the observed pattern is the result

of poor cooling in the beam and a concomitant ISR process, which acts to flip electron spins at a rate of 10^6/s or faster. What would be most illuminating at this point would be the deflection spectrum of VCl_4 vapor as an effusive beam at room temperature, for neither clustering nor static Jahn–Teller effects would be factors here, and the slow beam should show a large splitting if the molecule is free of ISR processes, but only broadening if the ISR processes are important. We have attempted this; however, the effusive beam intensity is below our sensitivity limits at the moment.

We conclude the following from these deflection experiments:

(1) Splittings within the magnetic deflection spectrum of a transition-metal compound seeded into a molecular beam of a rare-gas carrier may be seen even though the compound in the condensed phase shows very rapid spin–lattice relaxation.

(2) Under the conditions prevailing in the Ar, Kr, and Xe beams, the electron spin of the VCl_4 molecule is not being relaxed at any significant rate ($<10^4$ s^{-1}) by Jahn–Teller driven nuclear motions. However, the cooling in these beams is strong enough to result in the significant formation of $(VCl_4)_x$ clusters, which are either diamagnetic or weakly paramagnetic. There is no further structure observed in the splitting pattern beyond that due to electron spin, suggesting either that only $N = 0$ rotational levels are populated in the expansion or, more likely, that any possible spin–rotation coupling within VCl_4 molecules having $N > 0$ is quenched by the Paschen–Back effect at the kilogauss fields in question.

(3) The lack of VCl_4 deflection when seeded into the He beam in large part is due to the high velocity of the carrier gas; however, this does not explain the observed result quantitatively and a rapid ISR ($\tau = 10^{-6}$ s) may be a factor here. Though our results can be accomodated by the ISR theory, they must not be construed as proving the reality of this hypothesis.

(4) Any conclusive effects of ISR resulting from transitions between the Jahn–Teller minima of VCl_4 are not visible in the seeded beams used here but may appear in the deflection spectrum of an effusive beam of the compound, in which there is a low beam velocity and no complications from either clustering or cooling.

(5) Possible clustering of a paramagnetic species with the carrier gas can be ascertained by determining that the observed deflections in different carrier gases scale inversely with the squares of the measured beam velocities, for only at constant mass of the deflected particle does this inverse-square relationship hold. Alternatively, for a beam generated using any one carrier gas in which the paramagnetic molecule M and the rare gas RG combine to form $M \cdot RG_x$ mixed clusters all moving with the same velocity, the SG deflections will scale directly with the inverse masses of the clusters.

Time-Resolved Unimolecular Dissociation of Styrene Ion. Rates and Activation Parameters

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Abstract: The rate of unimolecular dissociation of styrene ion into benzene ion plus acetylene was measured by time-resolved photodissociation at 308 nm in the ICR ion trap. A rate constant of 1.10×10^5 s^{-1} was obtained at a total ion internal energy of 4.20 eV. Using accurate heat of formation data for the reactant and products, a 0 K reaction enthalpy of 2.42 eV was assigned. RRKM rate–energy curves were calculated for comparison with the present measurement and with previous photoionization coincidence (PEPICO) data. The shape of the RRKM curve matches experiment, and quantitative rate agreement is obtained assuming an activation energy of 2.32 eV and a tight transition state. The activation parameters derived from the activated complex, $\Delta S^{\ddagger}(1000 \text{ K}) = -6.4$ eu and $A_{\infty}(1000 \text{ K}) = 2.3 \times 10^{12}$ s^{-1}, are compared with values for other ion dissociations and with neutral-molecule rearrangements and rearrangement dissociations.

A body of precise and reliable kinetic information on the unimolecular dissociation of energy-selected low-pressure gas-phase

ions has become available through several new techniques. Moreover, the basis for making the connection and comparison