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VCl_4 Revisited: ESR and Photolysis in Solid Hydrogen, Neon, and Argon; Formation of VH_4

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Electron -spin-resonance (ESR) spectra of the VCl_4 molecule were observed at low concentrations at 2−4 K in solid H_2, D_2, Ne, and Ar. As previously observed in other matrixes, the spectra of an axial molecule were obtained in H_2, D_2, and Ne, indicative of a Jahn−Teller (JT) distorted molecule with compressed tetrahedral D_{2d} symmetry. However, in argon, a composite of an axial and a near-isotropic spectrum was observed, and annealing yielded only the isotropic at 4 K. This surprising result is discussed relative to JT dynamic vibronic interaction. Photolysis of VCl_4 in H_2 (and D_2) matrixes yielded a new spectrum assigned to VH_4 (or VD_4), indicating that the tetrahydride is also a JT-distorted ^2E ground-state molecule, in accord with earlier ab initio theory.

Introduction

The VCl_4 molecule has been experimentally[1−8] and theoretically[9−17] studied for more than 30 years with no definite conclusion as to the degree of vibronic coupling occurring in the ground state. Tetrahedral ligand field theory splits the ^2D term of the d^1 configuration into the orbitally degenerate ^2E lower state and ^2T upper state, separated by about 1 eV. These states are subject to vibronic distortion due to the Jahn−Teller (JT) effect. In JT terms, it is an $E \otimes e$ type with stabilization of a distorted tetrahedron in the ground state. (Renewed interest[18] in JT systems includes multimode effects in the $E \otimes e$ problem.)

VCl_4 was first treated theoretically by Ballhausen and Liehr in 1961[9] and subsequently by many workers culminating in the recent study of Stavrev and Zerner.[17] As those authors point out, the calculated Jahn−Teller stabilization energies given in the literature "vary from a few tens to a few thousands of wavenumbers".

Early electron-spin-resonance (ESR) spectra were measured by Herring, McDowell, and Nakajima,[4] by Pratt,[5] and by Johannesen, Candela, and Tsang.[6] The matrixes used in these cases were solid krypton and xenon,[4] solid mineral oil, CCl_4, *n*-heptane, $TiCl_4$, and $SnCl_4$,[5] and solid $TiCl_4$,[6] respectively, all at liquid helium temperatures at several microwave frequencies. Later (1981) studies by Ammeter et al.[7] were made in solid CCl_4, CBr_4, cyclohexane, and toluene at 4 K. Those authors were specifically concerned with the influence of molecular host lattices on the electronic properties of orbitally (near-) degenerate transition metal complexes. They conclude that there was little matrix dependence observed in the case of VCl_4. Agresti, Ammeter, and Bacci (in 1984)[8] again note that in a large variety of host systems showing resolved vanadium hyperfine structure the ESR spectra of VCl_4 are very similar and can be fitted with an almost axial spin Hamiltonian, whereby $g_{\parallel} = 1.95 \pm 0.01$, $g_{\perp} = 1.91 \pm 0.01$, $A_{\parallel} < 50$, $A_{\perp} = 105 \pm 10 \times 10^{-4}$ cm^{-1}. (The spectrum they are referring to is essentially the same as we find in solid hydrogen, illustrated here in our Figure 1, to be discussed below.) Pratt[5] has probably made the most thorough ESR studies. The spectra in $TiCl_4$ and $SnCl_4$ were anomalous in that they were not reproducible, and he concluded that they were "quite subject to intermolecular effects from the surrounding matrix". Overall, the ESR evidence at low temperatures find $g_{\parallel} > g_{\perp}$, indicating that the JT distortion stabilizes a flattened tetrahedron (D_{2d} symmetry). At higher temperatures, the spectrum reversibly disappears due to spin relaxation.

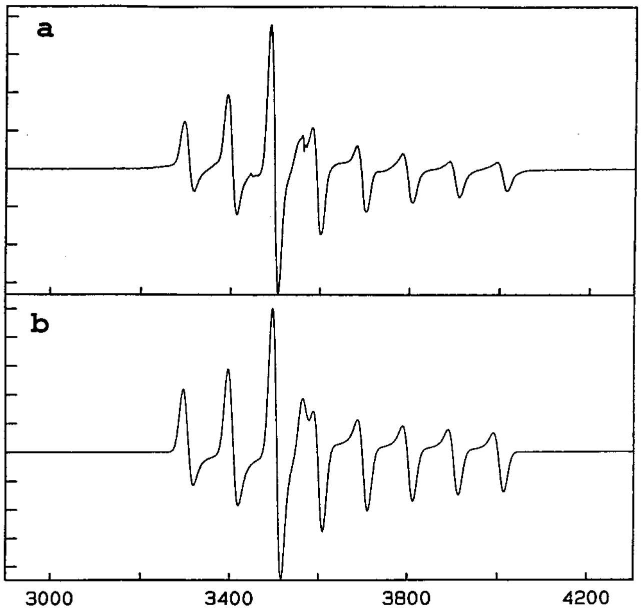

Figure 1. (a) ESR spectrum of 0.5% VCl_4 in a *n*-H_2 matrix at 2 K (ν = 9.806 GHz). (b) Simulated spectrum using $g_{\perp} = 1.917$, $g_{\parallel} = 1.952$, $A_{\perp} = 101$ G, $A_{\parallel} = 55$ G, and a Gaussian line width of 20 G.

An electron diffraction study[3] has found the V−Cl bond distance to be 2.14 Å, and several, not entirely conclusive, infrared and Raman measurements have been made.[1,2] The frequency most relevant to this research is ν_2 (the e bending) estimated[3] to be 97 ± 9 cm^{-1}.

The motivations for this ESR research on the VCl_4 molecule were the following: (1) to observe the molecule in the least perturbing solid environments, not previously employed; (2) to observe the spectra at higher resolution and possibly detect chlorine hyperfine structure—this latter was not realized; (3) to explore further ESR in the solid hydrogens;[19−21] and (4) to take

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advantage of the strong absorption of visible light by VCl_4 to anneal the matrixes and ultimately to photolyze the molecule.

Here we compare X-band ESR spectra of VCl_4 in hydrogen, deuterium, neon, and argon matrixes prepared at 2 or 4 K. The usual axial spectrum was obtained in most matrixes, but annealing and photolysis provided some interesting new results.

Experimental Section

Vanadium tetrachloride is a volatile red/brown liquid with a melting point of −26 °C. The VCl_4 was purified by pumping on the sample during freeze/thaw cycles to remove chlorine and hydrogen chloride impurities. This was achieved using a methyloxybenzene (anisole) slush bath at −37.5 °C where the vapor pressure of VCl_4 is ~0.1 Torr. Premixed samples of 4 and 0.5 mol % VCl_4 with host gases were prepared in 5 L bulbs, passed up through the ESR cavity and deposited onto the copper rod at 2 K or 4 K. Gas mixtures were prepared and used the same day. Another procedure involved the co-deposition of the VCl_4 and the matrix gas. The VCl_4 was introduced into the flowing matrix gas through a PTFE needle valve with the VCl_4 liquid at room temperature or cooled with either the anisole slush or the ice water slush. When co-deposited, the concentration of VCl_4 in the matrix could only be judged approximately by comparison of the observed ESR spectrum with the premixed spectra.

The matrixes were prepared on a copper rod (spatula-shaped) at 2−4 K, which was then lowered into a Bruker (ESP 300 E) X-band cavity. The ESR apparatus and accompanying cryogenics have been previously described.[22,23]

Samples isolated in neon or argon matrixes were annealed by either restricting the flow of liquid helium or by irradiating the sample with diffused unfiltered light from a 1 kW Xe/Hg lamp (Oriel) through the slotted side of the X-band cavity. During the annealing cycles ESR spectra were recorded at various temperatures. Photolysis, and the appearance of new spectral features, resulted when the lamp was focused on the cavity.

Vanadium tetrachloride was purchased from Aldrich with a purity of >98% based on chlorine analysis. Research grade argon (99.999%) was from B. O. C., neon (99.9995%) from Matheson, deuterium (99.6%) from Cambridge Isotope Laboratories, and hydrogen (99.9995%) from Matheson.

Results

All of the ESR spectra in H_2, D_2, and Ne, upon trapping at 2 K, were similar to that shown in Figure 1, which is also similar to previously measured spectra. The spectrum in solid H_2 was simulated as an axial doublet radical using Gaussian-shaped lines of line width 20 G, with $g_\perp = 1.917$ and $g_\parallel = 1.952$ and ^{51}V ($I = 7/2$) hyperfine pattern of eight lines yielding $A_\perp = 101$ G and $A_\parallel = 55$ G. These parameters are in general accord with earlier observations along with those derived from the spectra in other matrixes. Annealing of these solids on the Cu rod is difficult and usually led to the loss of the matrixes in the cases of H_2 and D_2, however, an effect was observed in neon (see below).

The ESR spectrum of 4% VCl_4 in argon at 4 K is the usual axial spectrum but with broadened lines. However, 0.5% VCl_4 in argon at 4 K yielded the more complicated spectrum shown in Figure 2. Upon annealing, this spectrum is revealed to be a composite of the axial spectrum (similar to Figure 1) and the narrower, nearly-isotropic spectrum shown in Figure 2 again measured at 4 K. This "isotropic" spectrum was obtained after either thermal annealing at ~30 K or after diffuse light absorption from the Xe/Hg lamp. The spectrum in Figure 2 could be simulated as a composite of the anisotropic and isotropic spectrum, as that figure indicates. Since this isotropic spectrum had apparently not been observed before in any other matrix, it is significant and needs rationalization.

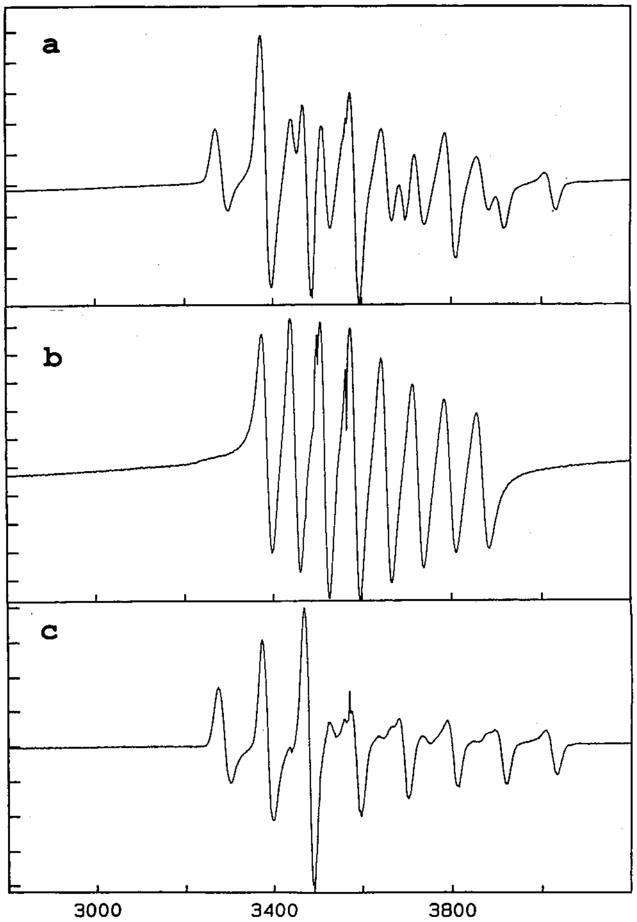

Figure 2. ESR spectrum of 0.5% VCl_4 in an argon matrix at 4 K ($\nu = 9.8064$ GHz). (a) Prior to annealing; (b) after annealing to about 30 K; (c) Difference spectrum.

We worried that it might be due to an impurity; however, this seems to be unlikely. First, it was completely reproducible through several runs where diligence was paid to the freeze−thaw of the VCl_4 liquid just before the experiment. Then, any impurity would have to be derived from the argon, which is research grade. Also, the axial VCl_4 signal is initially of the same order of intensity as the isotropic, and it appears that warming to just 30 K causes it to be converted to isotropic. This small temperature change is not conducive to chemical reaction but is to rearrangement of the argon matrix. The implication is that the sites for VCl_4 have altered in the matrix, leading to effectively an alteration of its JT behavior, indeed, almost to an isotropic spectrum of a tetrahedral VCl_4 radical! This is supported by the results in solid neon where some degree of annealing was successful. The original axial spectrum was altered with a narrowing of the spectra and the appearance of isotropic features (see Figure 3).

Photolysis of VCl_4 in Solid H_2 and D_2. Direct exposure to the focused light from the Xe/Hg lamp led to rapid photolysis, either the appearance of new spectra (in H_2, D_2) or only the disappearance of the VCl_4 spectrum (in Ne, Ar). Also, photolysis of VCl_4 in a 5% mixture of H_2/Ar led only to the gradual disappearance of VCl_4 signals, but a new spectrum was not observed. The immediately noticeable effect of photolysis on

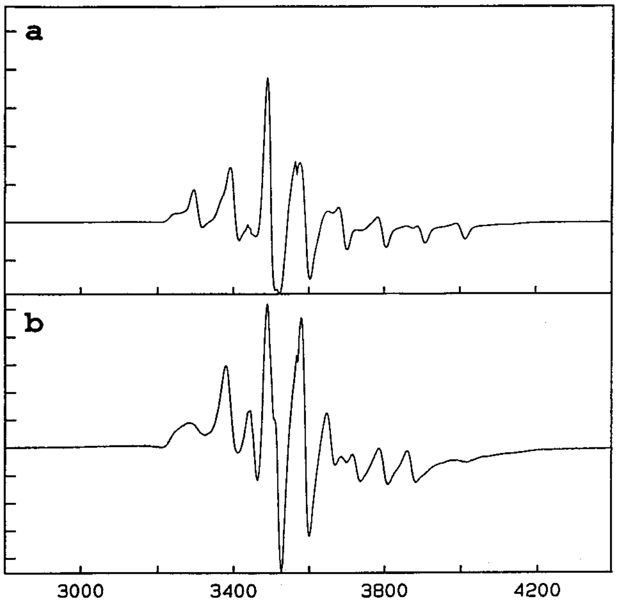

Figure 3. ESR spectrum of 0.5% VCl_4 in a neon matrix at 2 K (ν = 9.8057 GHz). (a) Prior to annealing; (b) after annealing. The feature at about 3200 G is a background signal.

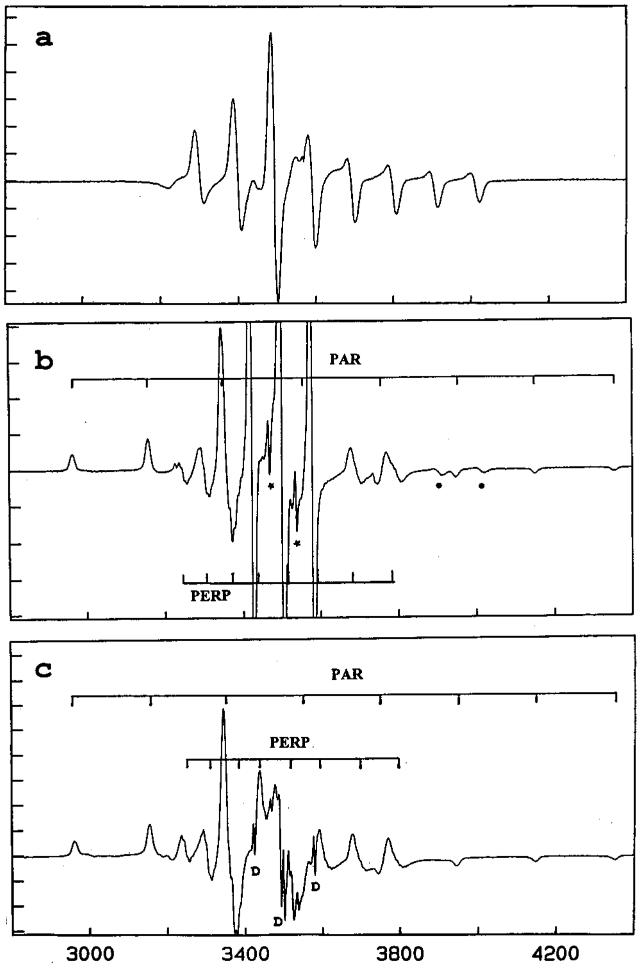

Figure 4. (a) ESR spectrum of 0.5% VCl_4 in a D_2 matrix at 2 K (ν = 9.8055 GHz). (b) Spectrum produced after photolysis of the matrix with a Xe/Hg lamp for 15 min. The three lines split by 80 G are due to D atoms, and (*) the sharp lines are due to CH_3 radicals. (•) Lines are believed to be unreacted VCl_4. (c) Spectrum produced by annealing to about 4 K.

the ESR spectrum was the appearance of three weak phase-down lines at high fields (between 3900 and 4400 G), two medium intensity lines phase-up at low field (between 2950 and 3200 G), an intense line mostly phase-up at ~ 3350 G, and two medium strength phase-up lines separated by 90 G between 3550 and 3700 G. The low-field and high-field lines have the form of "parallel" lines in matrixes containing randomly oriented radicals (see Figure 4).[24] These lines appear in both solid H_2 and solid D_2, slightly shifted between the two matrixes. The photolysis also produces H (and D) atom signals. The D atom signals are seen as the three sharp lines separated by about 80 G in Figure 4.

Discussion

In solid hydrogen, presumably the least perturbing matrix, an axial spectrum is obtained. at 2 K. Thus, VCl_4 is a distorted JT molecule, which at 2 K is static, implying that $E_{JT} > h\omega$; how much greater is the question. This behavior is apparently true in most other solids: mineral oil, CCl_4, cyclohexane, heptane. However, it is not true in argon and neon where both the anisotropic and the isotropic spectrum are observed at 2−4 K (as shown in Figures 2 and 3). Thus, contrary to earlier generalities, VCl_4 is influenced by the environment. Annealing in solid argon, and less certainly in neon, produces new sites in which dynamic effects appear.

"Isotropic" Spectrum in Argon. The spectrum is like that of a slowly tumbling molecule with increasing line width at the higher fields (or higher m_I values). It can be simulated using g = 1.93 and A = 69 G, and with the estimated line widths varying quadratically with m_I according to

$$22 - 1.5m_I + 0.5m_I^2$$

However, it is unlikely that VCl_4 is slowly tumbling in Ar at 4 K.

VCl_4 is a large molecule relative to substitutional sites in any of these matrix lattices. The V−Cl bond distance[3] is 2.14 Å, but a van der Waals radius for Cl must be added to that. If this is assumed to be 1 Å, the diameter of a VCl_4 sphere is about 6 Å. The diameter of a neon or argon atom in the face-centered-cubic lattice is 3.16 or 3.76 Å, respectively,[25] much too small to accommodate a VCl_4 molecule. p-H_2 crystallizes in a hexagonal-closed-packed lattice with 3.78 Å as the nearest-neighbor distance.[26] It is clear that VCl_4 would not fit into any of these crystalline lattices, and it is either accommodated by the packing of matrix atoms about it or fitted in the spaces between crystallities in the polycrystalline matrix. At 4 K it is then unlikely that rotational motion could occur.

O'Brien[27] has shown that the Jahn-Teller effect can also produce line-width variations at low temperatures, also depending upon $\Delta g = g_{\parallel} - g_{\perp}$ and $\Delta A = A_{\parallel} - A_{\perp}$. She has considered the relaxation due to transitions between vibronic levels where the "relaxation process will take the system from the ground state in one potential minimum to another by way of the excited states, even if the probability of direct transitions is small. At each of these transitions, the Larmor frequency of the system is changed but the electron spin is not turned over." Furthermore, if this relaxation process is dominant, she finds that the width of each of the ESR lines should be a multiple of

$$\tau[(g_{\parallel} - g_{\perp})\beta H + (A_z - A_x)I_z]^2/h^2$$

where τ is the relaxation time, i.e., a quadratic function of the m_I values (as in slow tumbling). (Δg is positive here but ΔA is negative.) Her discussion is related to the change in the anisotropic spectrum to an isotropic one as the temperature is changed. Here, there is no temperature change (the spectra are all measured at 2−4 K), but an environmental change in the matrix. One then postulates that annealing has either lowered the barriers between the three troughs or has changed the site where one trough is lower in energy, i.e., favored (sometimes referred to as nonrandom strain), to equalize all three and effectively allow tunneling to produce the "isotropic" spectra.

The warping, due to second-order effects, resulting in three troughs in the lower potential curve of the "Mexican hat", is characterized by a parameter β such that 2β is the height of the barrier between troughs.[28,29] β depends on both the linear and nonlinear vibronic coupling and is difficult to estimate in general, and more so for VCl_4 since there are no analogies as occur among ionic crystals. These matrixes, as originally formed, are usually "strained" as is evident by the change in the spectrum of a dopant after annealing. The relaxation of the matrix atoms about the isolated dopant often leads to loss of some sites and strengthening of more stable ones. These changes effect the change from the axial spectrum to the isotropic one in Figure 2, which apparently also occurs in neon.

A feature that is brought out by the simulation of this near-isotropic spectrum is the necessity of using Lorentzian rather than Gaussian line shapes, particularly to reproduce the outer wings of the spectrum. This is unusual in matrixes where lines are usually inhomogeneously broadened by the overlap from several sites. It implies that the spectrum is observed of molecules in uniform sites in the annealed argon matrix or perhaps that the dynamics have produced such an effect.

One can suggest that the barrier to fluxional behavior in VCl_4 is actually sensitive to the surroundings. Note that argon and neon are the least polar and polarizable of the matrixes in which VCl_4 has been studied. Solid p-H_2 would provide an even less perturbing environment, but normal H_2 was used here as a matrix. n-H_2 contains 75% o-H_2 molecules which possess an electric quadrupole moment.

Formation of VH_4. The photolysis of VCl_4 in H_2 or D_2 caused its disappearance and the appearance of a characteristic spectrum of another tetrahedral tetravalent molecule distorted to D_{2d} symmetry by the Jahn−Teller effect. The emerging spectrum in Figure 4 has the same features as $V(NEt)_4$,[30] $V(OBu)_4$,[31] and NbD_4.[32] This has been discussed rather thoroughly in our paper on the niobium tetrahydride.[32] Because of the disappearance of the VCl_4 spectrum, the appearance of atomic H, and the matrix environment of only solid hydrogen, the photolysis product is assigned to VH_4. (Note that the spectrum of VH_2 has been observed,[33] and it is not present.) Ab initio theory by Hood, Pitzer, and Schaefer[34] predicted (in 1979) a ^2E ground state for VH_4 with $r_e = 1.637$ Å and that "VH_4 could be prepared in the laboratory."

Most of the parallel lines in Figure 4, and in the corresponding spectrum in H_2, can be assigned, yielding $A_{\|} = 203(1)$ G, $g_{\|} = 1.901(5)$ for VH_4 and 198.4 (2) G, $g_{\|} = 1.914(5)$ for VD_4. The perpendicular lines are grouped between 3250 and 3750 G for VH_4; the intensity of the line at 3350 G is attributed to the near coincidence of the $m_I = +^3/_2$ parallel and perpendicular lines (similar to the strength of that line in VCl_4; this similarity is considered to be completely fortuitous.) The splittings among the perpendicular lines appear to increase in increasing magnetic field, i.e., the second-order terms are significant. $A_{\perp} \cong 78(1)$ G, $g_{\perp} \cong 1.985(5)$. Here as is NbH_4, $g_{\perp} > g_{\|}$, not as in VCl_4. That anomaly for VCl_4 has been noted earlier and attributed to different couplings to excited states.[32,34] The observed and calculated lines are listed in Table 1, along with the derived magnetic parameters.

TABLE 1: Analysis of the ESR Spectra Assigned to VH_4 and VD_4 as Axially Distorted Molecules at 2 K in the Solid Hydrogens

	parallel lines (G)		perpendicular lines (G)	
M_I (^{51}V)	obsd	calcd	obsd	calcd
	VH_4 ($\nu = 9.8052$ GHz)[a]			
+7/2	2974.3	2974.6		3243
+5/2	3170.6	3170.9	3301	3301
+3/2	3363.1	3369		3365
+1/2	3579.4	3569		3436.5
−1/2		3771		3515
−3/2	3976.1	3975	3600	3600
−5/2	4180.5	4180	3692.5	3692
−7/2	4389.0	4389	3791	3791
	VD_4 ($\nu = 9.8056$ GHz)[b]			
+7/2	2962.9	2962.8	3245	3244
+5/2	3156	3156	3301.5	3302
+3/2	3352.3	3352	3367	3367
+1/2		3548		3438
−1/2	3745.9	3747		3517
−3/2	3946.8	3947	3602	3602
−5/2	4148.4	4148	3692	3693
−7/2	4352.0	4352	3792	3792

[a] $A_{\|} = 202$ G, $g_{\|} = 1.901$, $A_{\perp} = 78$ G, $g_{\perp} = 1.984$. [b] $A_{\|} = 198.4$ G, $g_{\|} = 1.914$, $A_{\perp} = 78$ G, $g_{\perp} = 1.985$.

Conclusions

The observation of a reproducible almost-isotropic spectrum of VCl_4 is solid argon at 4 K indicates a dynamic Jahn−Teller effect. It suggests that the JT energy (and warping of the lower potential trough) is weak, i.e., comparable with the zero-point vibrational energy.

Excitation of VCl_4 in a hydrogen matrix leads to complete loss of the chlorine atoms, presumably to form HCl, and formation of VH_4. Theory[34] predicts VH_4 has a ^2E ground state, therefore, also subject to the Jahn−Teller effect. ESR measurements at 2 K confirm this by observation of the spectrum of an axial molecule, as expected of distorted VH_4 subject to a static JT effect.

Infrared spectra of these species in these matrixes are needed to verify these conclusions.

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