The σ Strength of Ligands Coordinated to Transition Metal Ions

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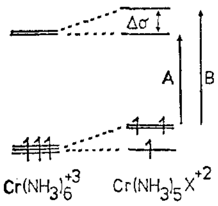
Abstract: The order of σ strength for coordinated halide ligands ($F^- > Cl^- > Br^- > I^-$) derived by analysis of the energies of the d-d transitions in Cr(III) complexes by Perumareddi and Schäffer is the opposite to that expected by many experimentalists. It is pointed out that this spectroscopic order is determined by variation in the energy of an empty metal-ligand σ antibonding orbital, whereas "normal" ideas concerning σ strength are concerned with variation in ground-state properties associated with the bonding orbitals. Using simple perturbation theory it is shown that a large destabilization energy of an antibonding orbital is not always matched by a proportionally large stabilization of the bonding partner. Crude calculations of the extended Hückel type support the perturbation analysis. They show specifically that, whereas the stabilization energy of the bonding e_g orbitals in CrF_6^{3-} is less than that in $CrCl_6^{3-}$, the opposite is true of the destabilization of the antibonding orbitals (mainly d_{z^2} or $d_{x^2-y^2}$). This provides a rationalization of the spectroscopic result. It is suggested that similar considerations should also apply to ab initio calculations.

Introduction

Among the various parameters which might be used as a measure of the σ strength of a ligand coordinated to a transition metal are the heat of formation of the complex and its stability constant. Good measures calculable using molecular orbital theory might be the stabilization energy of a σ donor orbital, the amount of charge donation, or the metal-ligand bond overlap population. One way a σ strength order has been experimentally evaluated is by an analysis of the transition energies arising from d-d promotion in substituted octahedral complexes[1,2] (**1**). The difference in energy between the two transitions A, B indicates quantitatively how effective various ligands X are in interacting with z^2 and perhaps how good a σ donor they are. The results are given in Table I. Some quantitative differences exist between the analyses of Perumareddi[1] and Schäffer[2] but in one sense both agree—the σ strength order arrived at by this route for the halogens is unmistakably $F^- > Cl^- > Br^- > I^-$. A similar order pertains in f orbital complexes.[3] This order is opposite to the one normally envisaged by experimentalists in the field of synthetic and structural chemistry. Iodide is generally considered a better σ donor than fluoride.



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This paradox is even more puzzling as a result of some simple extended Hückel molecular orbital (EHMO) calculations on transition metal complexes designed to simulate the behavior of z^2 when a Cl atom was substituted in $CrCl_6^{3-}$ to give $CrCl_5Y$.[4] On replacing a Cl^- ligand by a pseudoligand Y in which the s orbital ionization energy was increased by 5 eV and the p orbital ionization energy increased by 1 eV the energy of z^2 *rose*, i.e., replacing X by a ligand Y whose σ orbitals lay further away from the metal orbitals than those of X led to an *increase* in d orbital destabilization. Simulation of a poorer metal ligand interaction by allowing Y the same orbital ionization energies as Cl but decreasing the metal z^2-ligand s,p overlaps via an increase in orbital exponent led to the opposite result—a drop in the energy of z^2, i.e., a decrease in d orbital destabilization as expected. We show below how these results are connected and how σ strength is definition dependent and we unravel a novel molecular orbital effect.

Perturbation Treatment of Molecular Bonding

Second-order perturbation theory[5] tells us that the interaction energy of two orbitals φ_i and φ_j is given by

$$\epsilon_i^{(2)} = \frac{(H_{ij} - S_{ij}\epsilon_i^{(0)})^2}{\epsilon_i^{(0)} - \epsilon_j^{(0)}} \qquad (1)$$

where $\epsilon_i^{(0)}$ and $\epsilon_j^{(0)}$ are their unperturbed energies and S_{ij} is the overlap integral between them. Using the Wolfsberg-Helmholtz relationship for H_{ij}

$$H_{ij} = 1/2K(H_{ii} + H_{jj})S_{ij} \qquad (2)$$

and putting $K = 2$ we find

$$\epsilon_i^{(2)} = \frac{H_{jj}^2 S_{ij}^2}{\epsilon_i^{(0)} - \epsilon_j^{(0)}} \qquad (3)$$

where we identify $\epsilon_i^{(0)}$ with H_{ii}. If $|H_{ii}| > |H_{jj}|$ then this second-order correction is the stabilization energy of the in-phase (bonding) combination. The destabilization energy of the out of phase (antibonding combination) is simply given by

$$\epsilon_j^{(2)} = \frac{H_{ii}^2 S_{ij}^2}{\epsilon_j^{(0)} - \epsilon_i^{(0)}} \qquad (4)$$

Since $H_{ii}^2 > H_{jj}^2$ the bonding orbital will be stabilized less than the antibonding orbital is destabilized. In the absence of overlap in eq 1 then the interaction energies are equal:

$$\epsilon_j^{(2)} = -\epsilon_i^{(2)} = \frac{(H_{ii} + H_{jj})^2 S_{ij}^2}{\epsilon_j^{(0)} - \epsilon_i^{(0)}} \qquad (5)$$

Table II shows values of some computed molecular parameters for CrX_6^{3-} (X = F, Cl) systems where we have used the extended Hückel method to derive energy levels and coefficients. The parameters used are given in the Appendix. There are perhaps two qualitative feelings chemists have for the extent of interaction of two orbitals. The larger the overlap or the closer the orbitals are in energy the larger the interaction. This is sometimes expressed algebraically by the formula $S^2/\Delta\epsilon$ where $\Delta\epsilon$ is the orbital energy separation. Although implicit in molecular orbital calculations, the other parameters of eq 3 and 4 are not usually considered in qualitative arguments. On energy gap ($\Delta\epsilon$) grounds we suspect that metal-Cl interaction will be larger than for metal-F interaction (see Table III for values of the IPs). Even if overlap is included

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Table I. (I) Perumareddi's $\Delta\sigma$ Scale[1] in $Cr(NH_3)_5X^{2+}$ Complexes and (II) Schaffer's Scale[2] in Related Cr^{III} Systems

	(I),[a] μm^{-1}	(II), μm^{-1}
CN	0.131	
NH_3	0	2.111 ± 0.007 (0)[b]
*N*CS	−0.1	
H_2O	−0.11	2.37 ± 0.18 (+0.086)
N_3^-	−0.136	
F^-	−0.141	2.216 ± 0.020 (+0.035)
Cl^-	−0.212	1.663 ± 0.041 (−0.15)
Br^-	−0.251	1.476 ± 0.027 (−0.212)
I^-	−0.297	
py		1.754 ± 0.027 (−0.119)

[a] Relative to NH_3. (These values are the $\Delta\sigma$ of **1**.) [b] Here the values of scale II in parentheses are adjusted so as to be directly comparable with those of scale I. The larger values represent the absolute size of the σ contribution to the e_g/t_{2g} separation in the octahedral complex.

$S^2/\Delta\epsilon$ is still larger for the Cl 3s-metal interaction (Table II) even though S(metal z^2-F 2s) is larger than the corresponding term for the Cl system. Inclusion of the H_{ii}^2 and H_{jj}^2 terms, however, as in eq 3 and 4, changes things dramatically. For the bonding orbitals the same value of H_{ii} (−11.5 eV) is included for both types of interaction in M-Cl and M-F systems and thus our $S^2/\Delta\epsilon$ type arguments do hold here when we try to rationalize the relative sizes of the interactions. But for the antibonding orbitals the metal-F 2s interaction is favored over the metal-Cl 3s interaction by a factor of $(40)^2/(30)^2$ via inclusion of the H_{jj}^2 terms which are different for the chloride and fluoride cases. This is sufficient to push z^2 to higher energy in the CrF_6^{3-} than in the $CrCl_6^{3-}$ system. Thus fluoride is the stronger σ ligand measured by the elevation of z^2 but chloride is the stronger σ ligand measured by considering the properties of the bonding orbitals and, also shown in Table II, bond overlap populations and charges. (The last two properties also include the interactions of ligand orbitals with the metal s,p orbitals. An analysis of these interactions along similar lines to the above gives a similar result, larger stabilization energies of the bonding orbitals for the metal-chlorine interaction.) The total "heat of formation" of the chloro complex is also larger than that for the fluoro analogue.

Changes in Orbital Parameters

Let us now investigate the effect on the orbital energies of changing either the ionization potential or overlap integral of one or more ligands of the octahedral complex by looking initially at the first-order energy correction. The perturbed energy is simply given by

$$\epsilon_k^{(1)} = \sum_{i,j} (H_{ij}' - \epsilon_k^{(0)} S_{ij}')c_{ik}c_{jk} \tag{6}$$

where the primes represent the perturbation applied to H and S. For a two-orbital system the correction due to a change in overlap integral is given by

$$\begin{aligned}\epsilon_k^{(1)} &= (2.1/2K(H_{ii} + H_{jj})\Delta S_{ij} - \epsilon_k^{(0)}\Delta S_{ij})c_{ik}c_{jk} \\ &= (K[H_{ii} + H_{jj}] - \epsilon_k^{0})c_{ik}c_{jk}\Delta S_{ij} \end{aligned} \tag{7}$$

by using the Wolfsberg-Helmholtz approximation for H_{ij}. The term in parentheses is usually negative since $|K[H_{ii} + H_{jj}]| > |\epsilon_k^0|$ for chemically significant cases. Thus if k is a bonding orbital ($c_{ik}c_{jk}S_{ij} > 0$), $\epsilon_k^{(1)}$ is negative for an increase in overlap, i.e., an increase in stabilization. If k is an antibonding orbital ($c_{ik}c_{jk}S_{ij} < 0$), $\epsilon_k^{(1)}$ is positive, i.e., an increase in destabilization, on increasing overlap. This result is one we feel intuitively comfortable about; a larger "interaction" between two orbitals makes the in-phase combination more stable and the out of phase combination less stable.

Table II. Results of Perturbation and EHMO Calculations on CrX_6^{3-} (X = Cl, F)

A. Calculated using Perturbation Theory (eV)

		chlorine		fluorine	
		3s	3p	2s	2p
	overlap (S) with z^2	0.1697	0.1697	0.2038	0.1427
	$S^2/\Delta\epsilon$	0.001 557	0.008 228	0.001 457	0.003 085
stabilization of bonding orbital	$S^2H_{jj}^2/\Delta\epsilon$	0.21	1.09	0.19	0.41
	total	1.30		0.60	
destabilization of antibonding orbital	$S^2H_{ii}^2/\Delta\epsilon$	1.40	1.85	2.33	1.01
	total	3.25		3.34	

B. From EHMO Calculations

	chlorine	fluorine
destabilization of z^2 in CrX_6^{3-}	7.389 eV	8.263 eV
stabilization of ligand σ(s),a_{1g}[a]	0.2442 eV	0.1212 eV
stabilization of ligand σ(p),t_{1v}[a]	1.0448 eV	0.3564 eV
sum ligand σ stabilization	1.2891 eV	0.4776 eV
M-X bond overlap population	0.2646	0.1154
charge donated	0.29	0.12

[a] Relative to X_6^{6-}.

Table III

	orbital	H_{ii}, eV	exponent
Cl	3s	−30.0	2.033
	3p	−15.0	2.033
F	2s	−40.0	2.245[a]
	2p	−18.1	2.245[a]
Cr	4s	−9.00	1.700
	4p	−5.00	1.700
	3d	−11.50	4.95 (0.4876), 1.60 (0.7205)[b]

[a] Note that this is not the Slater exponent (2.600). Z^2 is destabilized less in CrF_6^{3-} than in $CrCl_6^{3-}$ for values of the exponent greater than about 2.3 for our choice of bond lengths, metal exponents, etc. [b] A double ζ function was used for these orbitals; coefficients in parentheses.

For a change in diagonal matrix element, however, the situation is a little more complex. Equation 6 becomes

$$\epsilon_k^{(1)} = \Delta H_{ii}c_{ik}^2 + 2\Delta H_{ij}c_{ik}c_{jk} \tag{8}$$

Making use of the Wolfsberg-Helmholtz approximation gives

$$\epsilon_k^{(1)} = \Delta H_{ii}(c_{ik}^2 + Kc_{ik}c_{jk}S_{ij}) \tag{9}$$

For the bonding combination c_{ik}^2, $c_{ik}c_{jk}S_{ij} > 0$ and as $|H_{ii}|$ increases the bonding combination drops to lower energy. The *stabilization energy* of the bonding orbital will, however, only increase if the inequality (eq 10) holds

$$c_{ik}^2 + Kc_{i}kc_{jk}S_{ij} > 1 \tag{10}$$

which, since the orbital is normalized

$$c_{ik}^2 + c_{jk}^2 + 2c_{ik}c_{jk}S_{ij} = 1 \tag{11}$$

implies

$$c_{jk}^2 + (2 - K)c_{ik}c_{jk}S_{ij} < 0 \tag{12}$$

which is never true for normal usage of K(1.5–2.0).

For antibonding orbitals $c_{ik}c_{jk}S_{ij} < 0$ and so $\epsilon_k^{(1)}/\Delta H_{ii}$ from eq 9 may be either positive or negative depending on the relative sizes of the two terms in parentheses in eq 9. Substitution of some numerical values into these equations shows clearly these two cases.

For $CrCl_6^{3-}$,"z^2" is given from our crude molecular orbital calculation as

$$\psi = 1.0512\phi_{z^2} - 0.2205\phi_{\mathrm{sL}} + 0.3203\phi_{\mathrm{pL}} + \sum_{\substack{\text{other five}\\ \text{ligands}}} c_i\phi_i \qquad (13)$$

where we focus on the interaction between z^2 and one ligand lying along the z axis. Using the overlap data from Table II eq 9 becomes

$$\epsilon_k^{(1)} = -\Delta H_{ii}^{\mathrm{s}} \times 0.020\,22 \qquad (14)$$

Thus increasing the ionization potential of the ligand s orbital leads to an *elevation* of z^2—the counterintuitive result. In a similar fashion we find eq 15 for a change in p orbital ionization potential.

$$\epsilon_k^{(1)} = \Delta H_{ii}^{\mathrm{p}} \times 0.002\,60 \qquad (15)$$

This is the exactly opposite (but intuitively satisfactory) result—as the p orbital ionization potential of the ligand is increased the energy of z^2 drops (by a smaller amount, however, than the elevation produced in z^2 by changing the ligand s orbital ionization potential). By increasing the metal-chlorine bond length to 2.4 Å we can change the overlaps and molecular orbital coefficients of eq 13 such that $\epsilon_k^{(1)}$ of eq 15 also contains a minus sign. So the usual way of simulating a more electronegative substituent by increasing $|H_{ii}^{\mathrm{p}}|$ by 1 or 2 eV will lead to *different* results on the energy of z^2 depending upon the geometrical (and presumably exponent choice) parameters of the system.

Combining the results of eq 14 and 15 we can see that on substitution of a Cl atom by F in $CrCl_6^{3-}$ on H_{ii} grounds alone z^2 is pushed up in energy since the energy change is dominated by the change in H_{ii}^{s}. On fluorine substitution the relevant overlap integrals also change (Table II); z^2-ligand s increases and z^2-ligand p decreases. We calculate from eq 7, 14, and 15 an elevation of z^2 of +0.3513 eV, i.e., on single fluorine atom substitution in $CrCl_6^{3-}$, z^2 rises in energy as indicated from the experimental data of Table I. (Second-order perturbation energy corrections are smaller and the gross up and down movement of z^2 is dominated by this first-order change.) We may therefore summarize:

(1) Increasing the metal d-ligand σ overlap integral leads to an increasing stabilization of the (ligand σ) bonding orbital and an increasing destabilization of the (d orbital) antibonding orbital.

(2) Increasing the ligand σ ionization potential usually leads to a decrease in the stabilization energy of the bonding orbital, but whether the change in energy of the antibonding orbital is positive or negative depends on the interplay of several factors.

Discussion

We have used extended Hückel calculations to illustrate our point. This is a semiempirical method the results of which should not really be used quantitatively to weigh energetic effects in such different systems. Because we are at the mercy of the choice of molecular parameters the actual energy changes are not to be regarded as being accurate representations of what really happens in these CrX_6^{3-} complexes. However, they are sufficient for our purpose and indicate numerically the sort of effects that are predicted to occur using the perturbation approach. However, an exactly analogous effect is expected using ab initio and other methods where we are not restricted to one-electron models. This may be simply seen in qualitative terms by reworking the algebra above using the newly developed SCF partitioning scheme[6] of Whangbo, Schlegel, and Wolfe. Interestingly, effects exactly analogous to the ones we have been describing in EHMO calculations are found in CNDO calculations[7] on $CrCl_6^{3-}$ and CrF_6^{3-}. The effect is therefore certainly not restricted only to calculations of the extended Hückel sort.

There are of course some alternative explanations of the spectral observations. It could be argued that coordinated F^- carries a larger charge than Cl^- and thus the electrostatic (crystal field) contribution to the d orbital splitting energy is larger for F^- than for Cl^-. On a purely molecular orbital level the switching on of d-s mixing on loss of octahedral symmetry ($CrX_6 \rightarrow CrX_5Y$) may be significantly different for Y = F^- compared to Y = Cl^-. (d-s mixing has been used before[8] to rationalize results incompatible with a d orbital only model.) However, this explanation is invalid in the f orbital case (in O_h f orbitals transform as $a_{2u} + t_{1u} + t_{2u}$) where evaluation of the σ order[3] may be achieved by analysis of the MX_6 species itself without the need to lower the molecular symmetry. Finally Gerloch and Slade[9] illustrate some of the problems of interpretation in chemical terms of the parameters of simple models (crystal field or angular overlap) obtained from a spectral analysis. These clearly contain contributions from two-electron terms.[10] We now add to this list another possibility which we feel has merit in being simple and also semiquantitative.

σ donor strength, from our discussion above, is then very much definition dependent. From the calculations there is a larger stabilization of the σ framework, a larger charge shift, and larger M-X bond overlap population for $CrCl_6^{3-}$ than for CrF_6^{3-}, to be contrasted with the larger destabilization energy of the z^2 orbital in the fluoride complex. Thus by extrapolation of this result we may reconcile the result implied by analysis of the electronic spectra (σ strength order, $F^- > I^-$) with the usual feeling that it should be the reverse.

The result does have some far-reaching consequences. In inner sphere redox reactions of Cr^{II}/Cr^{III} systems, for example, the rate is faster with a Br^- ligand trans to the bridge in the acceptor (Cr^{III}) part of the molecule than with a F^- there. Conversely, with a F^- trans to the bridge on the donor side (Cr^{II}) the rate is faster than with Br^-. These results are rationalized[11] on the basis that F^- pushes up z^2 in energy more than does Br^-.

More particularly, calculations devised to study the structures of transition metal complexes focus on the d orbital region of the molecular orbital diagram. These orbitals are metal-ligand σ antibonding and (in the absence of π acceptor ligands) metal-ligand π antibonding. The analysis of ligand site preferences, the energetics of the system as the geometry changes, and relative orbital energies when the nature of the ligand(s) is changed will depend on the parameters used in the calculation perhaps to a larger extent than previously imagined. Interestingly we have quantitatively rationalized[12] the relative rates of ligand substitution in low-spin d^8 square planar Pt^{II} complexes as a function of the ligands present in the complex by using the data of Table I as a measure of metal d orbital-ligand σ interaction.

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Appendix

The parameters used in the extended Hückel calculations[13] are given in Table III. They are the sort of standard EHMO parameters used by a variety of authors in this field. The Cr-Cl and Cr-F bond lengths used were 2.32 and 1.95 Å, respectively.

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The Proton Chemical Shift in Polycrystalline $H_2Os_3(CO)_{10}$, $H_4Ru_4(CO)_{12}$, and $H_4Os_4(CO_{12})$

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Abstract: Multiple-pulse NMR techniques have been used to obtain estimates of the proton chemical shift tensors for protons directly bound to heavy metal atoms in $H_2Os_3(CO)_{10}$, $H_4Os_4(CO)_{12}$, and $H_4Ru_4(CO)_{12}$. The chemical shift anisotropy for these bridging protons was found to be less than 30 ppm, and the temperature-dependent spectra for $H_4Ru_4(CO)_{12}$ indicated the presence of anisotropic proton motion at room temperature.

Introduction

In recent years it has become possible to measure proton chemical shift tensors in solids by multiple pulse techniques.[1-6] Such measurements have included studies of organic compounds, hydrogen-bonded crystals, hydrated crystals, water itself, and one conducting system.[6] This paper reports proton chemical shift spectra for protons directly bonded to transition metals via metal-hydrogen-metal bridge bonds. In solution such compounds, in contrast to other materials studied, exhibit a large positive chemical shift. For example, in their review Kaesz and Saillant[7] cite an isotropic chemical shift range of $\tau \sim 15$-30 ppm ($\sigma \sim 5$-20 ppm) for hydrogens directly bonded to transition metals with those hydrogens bridging metal-metal bonds typically at even higher fields. The range for proton chemical shifts for organic liquids is typically $\tau \sim 0$-10 ppm ($\sigma \sim -10$ to 0 ppm) with similar isotropic values in the solid state.[1,2] An early theoretical prediction by Buckingham and Stephens[8] of the possibility of an unusually large chemical shift anisotropy for protons directly bonded to a transition metal (up to 500 ppm) has added speculation that such large upfield values for the isotropic values might be due to such large anisotropies.

Experimental Section

The spectra presented in this paper were obtained using a spectrometer[9] and an eight-pulse sequence[10] which have been discussed. A cycle time of 48 μs was used for results reported here, although some data were taken with a cycle time of 36 μs. It was necessary to signal average, and spectra were taken on both sides of resonance and reflected in order to determine the proper choice of phase. In some cases the resulting spectra were added to improve signal to noise. For $H_2Os_3(CO)_{10}$ and $H_4Ru_4(CO)_{12}$ runs were typically 1-2 h with 3-5-min pulse rates, while for $H_4Os_4(CO)_{12}$ data were accumulated over a 24-h period. Spin-lattice relaxation times ranged from somewhat under 1 min for the $H_4Ru_4(CO)_{12}$ to 5 min for the more rigid species, and pulse rates ranged from two to five times the relaxation time for a particular sample.

For temperature control a nitrogen-flow variable temperature probe was used, and the temperature was checked before and after each run and found constant to within ±1 K. An acetyl chloride sample in a sealed spherical NMR tube was used for tuning and confirming proper operation of the spectrometer since it is liquid over the temperature range of interest (liquid range: -112 to 50.9 °C). The chemical shift of acetyl chloride relative to a spherical sample of tetramethylsilane was determined at room temperature and the result used in assigning chemical shifts relative to tetramethylsilane at other temperatures.

In addition to studying the compounds under the eight-pulse sequence, two phase-altered[11] sequences were used, the effect of which is to sort out contributions to the line width coming from other than static field inhomogeneity.

The samples used in this study were kindly provided by Professor J. R. Shapley. They were prepared using the procedure of Knox et al.[12] and purified by chromatography on silica gel.

Results and Discussion

$H_2Os_3(CO)_{10}$. The structure of $H_2Os_3(CO)_{10}$ taken from the paper of Churchill, Hollander, and Hutchinson[13] is shown in Figure 1a. The molecule is composed of an isosceles triangle of osmium atoms with the proton pair bridging the base. The carbonyls in the isolated molecules are symmetrically arranged so that the protons are equivalent, and thus the multiple-pulse NMR spectrum of a polycrystalline sample would furnish a single proton chemical shift tensor. However, in the solid state the molecular packing distorts the carbonyls slightly, and there are two different kinds of protons. Since the packing distortions are small[13] and one does not expect intermolecular effects on the chemical shift tensor to be large, we have fit the spectra to a single proton chemical shift tensor. The fact that the isotropic chemical shift found ($\bar{\sigma}$ 9 ppm at 300 K and 11 ppm at 230 K) is close to the value observed in solution, $\bar{\sigma}$ 11.7 ppm (τ 21.7 ppm[12]), is evidence for the isolation of the molecular unit in the solid state.

Figure 2 shows the multiple pulse spectra for $H_2Os_3(CO)_{12}$ at 300 and 230 K along with the results of one of the phase-altered sequences.[10] The similarity of spectra taken at 230 and 300 K indicates that the protons are not involved in a motional process sufficient to average the spectrum differently at these temperatures. In addition to an anisotropy in the proton chemical shift tensor, a variety of other phenomena could be contributing to the observed line widths of the spectra in Figure 2. An estimate of factors contributing to the line width other than inhomogeneity broadening was obtained by performing

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