

## References and Notes

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## Correspondence

## Vibrational Frequency Shifts for Isotopes of Hexacarbonylchromium

AIC50651Y

Sir:

Recently Perutz and Turner<sup>1</sup> reported an interesting study of the infrared spectra of various isotopic species of  $\text{Cr}(\text{CO})_n(\text{C}^{13}\text{CO})_{6-n}$  isolated in a low-temperature matrix of  $\text{CH}_4$ . It is quite remarkable that they were able to fit 19 observed infrared-active CO stretching peaks with a mean error of  $0.3 \text{ cm}^{-1}$  and maximum error of  $0.9 \text{ cm}^{-1}$  using a "CO-factored force field". It is difficult to present an analytical explanation for the applicability of this approximate force field; however, it is apparent that the approximations are compensated for similarly for the various  $\text{Cr}(\text{C}^{12}\text{C}^{16}\text{O})_n(\text{C}^{13}\text{C}^{16}\text{O})_{6-n}$  isotopic species. The anharmonicities are also apparently distributed satisfactorily for this agreement.

In their text, Perutz and Turner stated that this agreement demonstrates "the model used in the calculations is valid...". They also stated "The force constants show that the Cotton-Kraihanzel (C-K) approximation  $2k_{\text{cis}} = k_{\text{trans}}$  holds well for all the hexacarbonyls." I believe these statements are misleading as they should include the qualification "for making frequency assignments for the  $^{13}\text{C}$ -substituted species." As the statements stand, they imply that the force field is chemically meaningful—it is much later in the paper that the authors mention the "lack of direct chemical meaning in the absolute values of the force constants (particularly the interaction constants)...."

The frequencies of  $^{18}\text{O}$  isotopic species show that there are serious limitations to the CO-factored force field. If the species  $\text{Cr}(\text{C}^{12}\text{C}^{16}\text{O})_n(\text{C}^{12}\text{C}^{18}\text{O})_{6-n}$  are included in such a calculation, the agreement is quite unsatisfactory, as can be seen from Table I. In the first column are given the observed frequencies<sup>2</sup> for  $\text{Cr}(\text{CO})_6$  in  $\text{CCl}_4$  solution. Column A gives the frequencies calculated using a CO-factored force field, refining the potential constants  $F_{\text{CO}}$ ,  $F_{\text{CO,C'O}}(\text{c})$ , and  $F_{\text{CO,C'O}}(\text{t})$  and using only the six CO stretching frequencies of  $\text{Cr}(\text{C}^{12}\text{C}^{16}\text{O})_6$  and  $\text{Cr}(\text{C}^{13}\text{C}^{16}\text{O})_6$ . One notes that the calculated values for the  $\text{E}_g$  mode and particularly the  $\text{A}_{1g}$  mode of  $\text{Cr}(\text{C}^{12}\text{C}^{18}\text{O})_6$  are far from the observed values. In column B are given calculated values from an attempt to fit all nine of the observed frequencies using a CO-factored force field. The  $\text{A}_{1g}$  and  $\text{E}_g$  modes of both the  $^{13}\text{C}$  and  $^{18}\text{O}$  species are in significant error. Column C gives the values calculated when the force constants are fixed at realistic values as estimated in ref 2 rather than being fixed at zero as for the CO-factored force field. Solution C, of course, shows much better agreement. The calculated values are listed for the pentasubstituted mixed isotopic species also. Though we do not have observed values for comparison, it is apparent that the different solutions give rather different values. One would expect column C to be more nearly correct than A or B.

It must be pointed out that anharmonicity has been neglected so that the values of the CO,C'O' interaction constants, even in column C of Table I, are not meaningful. The correct

Table I. CO Stretching Frequencies<sup>a</sup> and Calculated Force Constants<sup>a</sup> for Some Isotopic Species of  $\text{Cr}(\text{CO})_6$  in  $\text{CCl}_4$  Solution

	Obsd <sup>b</sup>	A	B	C
Frequencies				
$\text{Cr}(\text{C}^{12}\text{C}^{16}\text{O})_6$				
$\text{A}_{1g}$	2112.4	2111.5 <sup>c</sup>	2113.4 <sup>c</sup>	2113.0 <sup>c</sup>
$\text{E}_g$	2018.4	2017.8 <sup>c</sup>	2019.1 <sup>c</sup>	2018.7 <sup>c</sup>
$\text{F}_{1u}$	1984.4	1984.5 <sup>c</sup>	1984.8 <sup>c</sup>	1984.6 <sup>c</sup>
$\text{Cr}(\text{C}^{13}\text{C}^{16}\text{O})_6$				
$\text{A}_{1g}$	2063.6	2064.5 <sup>c</sup>	2066.3 <sup>c</sup>	2063.0 <sup>c</sup>
$\text{E}_g$	1972.3	1972.9 <sup>c</sup>	1974.1 <sup>c</sup>	1972.0 <sup>c</sup>
$\text{F}_{1u}$	1940.3	1940.2 <sup>c</sup>	1940.6 <sup>c</sup>	1940.1 <sup>c</sup>
$\text{Cr}(\text{C}^{12}\text{C}^{18}\text{O})_6$				
$\text{A}_{1g}$	2066.2	2060.5	2062.4 <sup>c</sup>	2066.2
$\text{E}_g$	1972.8	1969.1	1970.3 <sup>c</sup>	1972.5
$\text{F}_{1u}$	1937.6	1936.5	1936.9 <sup>c</sup>	1937.3
$\text{Cr}(\text{C}^{12}\text{C}^{16}\text{O})(\text{C}^{13}\text{C}^{16}\text{O})_5$				
$\text{A}_1$		2075.8	2077.6	2075.2
$\text{A}_1$		1994.2	1995.3	1994.0
$\text{A}_1$		1952.5	1953.0	1952.1
$\text{B}_2$		1972.9	1974.1	1972.0
$\text{E}$		1940.2	1940.6	1940.1
$\text{Cr}(\text{C}^{12}\text{C}^{16}\text{O})(\text{C}^{12}\text{C}^{18}\text{O})_5$				
$\text{A}_1$		2073.3	2075.1	2077.6
$\text{A}_1$		1992.4	1993.5	1994.6
$\text{A}_1$		1949.2	1949.7	1950.7
$\text{B}_2$		1969.1	1970.3	1972.5
$\text{E}$		1936.5	1936.9	1937.3
Force Constants				
$F_{\text{CO}}$		16.44	16.45	16.54
$F_{\text{CO,C'O}}(\text{t})^d$		0.53	0.54	0.26
$F_{\text{CO,C'O}}(\text{c})$		0.26	0.26	0.16
$F_{\text{MC}}$		[0] <sup>e</sup>	[0] <sup>e</sup>	[2.1] <sup>e</sup>
$F_{\text{MC,MC}}(\text{t})$		[0]	[0]	[0.4]
$F_{\text{MC,CO}}$		[0]	[0]	[0.69]
$F_{\text{MC,C'O}}(\text{c})$		[0]	[0]	[-0.09]
$F_{\text{MC,C'O}}(\text{t})$		[0]	[0]	[-0.10]
$F_\alpha$		[0]	[0]	[0.79]
$F_\beta$		[0]	[0]	[0.56]
Other $F_{ij}$		[0]	[0]	[0]

<sup>a</sup> Units are  $\text{cm}^{-1}$  for frequencies and are as given in ref 2 for force constants. <sup>b</sup> From ref 2. <sup>c</sup> These frequencies were used in refinement. <sup>d</sup> (t) is for trans; (c) is for cis. <sup>e</sup> Values in brackets were constrained for the calculations.

results<sup>2</sup> are  $F_{\text{CO,C'O}}(\text{t}) = 0.08$  and  $F_{\text{CO,C'O}}(\text{c}) = 0.17 \text{ mdyne}/\text{\AA}$ , bearing little resemblance to the results of Table I. It is clear that the CO-factored force field is indeed useful for assigning isotopic frequency shifts for the  $^{13}\text{C}$  isotope alone but not both the  $^{13}\text{C}$  and  $^{18}\text{O}$  isotopic species together.<sup>3</sup>

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**Registry No.**  $\text{Cr}(\text{C}^{12}\text{C}^{16}\text{O})_6$ , 13007-92-6;  $\text{Cr}(\text{C}^{13}\text{C}^{16}\text{O})_6$ , 25941-09-7;  $\text{Cr}(\text{C}^{12}\text{C}^{18}\text{O})_6$ , 25875-16-5;  $\text{Cr}(\text{C}^{12}\text{C}^{16}\text{O})(\text{C}^{13}\text{C}^{16}\text{O})_5$ , 53109-12-9;  $\text{Cr}(\text{C}^{12}\text{C}^{16}\text{O})(\text{C}^{12}\text{C}^{18}\text{O})_5$ , 58167-58-1.

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- (2) L. H. Jones, R. S. McDowell, and M. Goldblatt, *Inorg. Chem.*, **8**, 2349 (1969).
- (3) The following paper in this issue by Burdett et al. prompts me to make the following comment. The intent of this Note is not to criticize the use of  $^{13}\text{C}$  isotopic frequency shifts to deduce structural information. Its purpose is to caution against attempts at explaining the "CO-factored" interaction constants in terms of bonding theory. Perutz and Turner<sup>1</sup> have made the statement "...the approximation  $k'_{\text{cis}}(\text{eq-eq}) = 1/2k_{\text{trans}}$  holds very well both for  $\text{Cr}(\text{CO})_6$  and  $\text{Cr}(\text{CO})_5$ , as predicted also by the valence-shell force field." To me the intent of such a statement appears to be to offer experimental evidence which supports a theoretical model. It is such attempts at fitting bonding models to admittedly meaningless force constants which I wish to discourage.

Los Alamos Scientific Laboratory  
University of California  
Los Alamos, New Mexico 87545

Llewellyn H. Jones

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### Vibrational Frequency Shifts for Isotopes of Hexacarbonylchromium

AIC508466

Sir:

It is indeed surprising that for  $\text{Cr}(\text{CO})_n(\text{C}^{12}\text{O})_n(\text{C}^{13}\text{O})_{6-n}$  the fit of experimentally observed infrared bands and the theoretical spectrum, estimated from a CO-factored force field, is so very good.<sup>1</sup> In fact, there are some features of the vibrational data for  $\text{Cr}(\text{CO})_6$  and its isotopes which are even more surprising than Jones implies.<sup>2</sup> On a CO-factored force field, since the  $\mathbf{G}$  matrix is diagonal in the reduced mass of CO, complete replacement of  $^{12}\text{C}^{16}\text{O}$  by either  $^{13}\text{C}^{16}\text{O}$  or  $^{12}\text{C}^{18}\text{O}$  should shift all CO stretching bands by a factor of 0.9778 or 0.9759, respectively. In fact, from Jones' Table I, were obtained the values shown in our Table I. The difference between symmetry modes and from  $^{13}\text{C}^{16}\text{O}$  to  $^{12}\text{C}^{18}\text{O}$  is striking—this is also seen by refining the data. Using the energy-factored force field, Jones based his refinement on  $\text{Cr}(\text{CO})_6$  and  $\text{Cr}(\text{CO})_6$  (column A) and on  $\text{Cr}(\text{CO})_6$ ,  $\text{Cr}(\text{CO})_6$ , and  $\text{Cr}(\text{CO})_6$  (column B). The standard deviations between experimental and theoretical values for these calculations and also for refining on  $\text{Cr}(\text{CO})_6$  and  $\text{Cr}(\text{CO})_6$  and on  $\text{Cr}(\text{CO})_6$  and  $\text{Cr}(\text{CO})_6$  are

	12,16-	12,16-	13,16-	12,16-
	13,16	12,18	12,18	13,16-
$\sigma, \text{cm}^{-1}$	0.60	1.71	2.26	1.93

The reasons for these surprising differences do indeed lie in fortuitous or less fortuitous cancelation of terms; the details of these subtleties are discussed elsewhere.<sup>3</sup> One possibly significant observation is that use of the infrared-active frequencies only of  $\text{Cr}(\text{CO})_n(\text{CO})_{6-n}$  gives an excellent fit of the frequencies. Only when Raman-active modes are included, is the quality of the fit reduced when the frequency-factored force field is used.

However, we wish to point out that we are not primarily interested in the nuances of various force fields nor in the lack of chemical significance of the force constants obtained. Our major object is to use isotopic CO data to determine the structures of metal carbonyl and isolated fragments trapped in low-temperature matrices. Although recent theoretical work<sup>4</sup> confirms the structures determined experimentally, it is nonetheless intuitively surprising that  $\text{Co}(\text{CO})_4$  is  $C_{3v}$ ,<sup>5</sup>  $\text{Fe}(\text{CO})_4$  is  $C_{2v}$ ,<sup>6</sup>  $\text{Mo}(\text{CO})_4$  is  $C_{2v}$ ,<sup>7</sup> and  $\text{Cr}(\text{CO})_5$  is  $C_{4v}$  with a droop angle sensitive to the environment.<sup>8</sup> Confidence in

Table I

	$T_{1u}$	$A_{1g}$	$E_g$
$\nu[\text{Cr}(\text{CO})_6]/\nu[\text{Cr}(\text{CO})_6]$	0.9778	0.9769	0.9772
"Error", $\text{cm}^{-1}$	0.0	1.9	1.2
$\nu[\text{Cr}(\text{CO})_6]/\nu[\text{Cr}(\text{CO})_6]$	0.9764	0.9781	0.9774
"Error", $\text{cm}^{-1}$	-1	-4.6	-3.0

such structures is surely dependent on the match in both position and intensity of experimental and theoretical isotope patterns. The  $\text{Cr}(\text{CO})_6$   $^{13}\text{C}$  data were reproduced<sup>1</sup> to demonstrate how well the data can be fitted with a CO-factored force field for a molecule whose structure is not open to question. The bounds of reliability of such calculations are discussed at length elsewhere.<sup>3</sup> Suffice it to say that  $^{13}\text{C}$  substitution *does* lead to reliable structural information where a full vibrational analysis is impossible.

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Registry No.  $\text{Cr}(\text{CO})_6$ , 13007-92-6.

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Department of Inorganic Chemistry  
The University  
Newcastle upon Tyne, NE1 7RU, England

J. K. Burdett\*  
R. N. Perutz  
M. Poliakoff  
J. J. Turner

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### Carbon-13 Isotopic Exchange in Pentacarbonyliron

AIC50404U

Sir:

It has already been exhaustively proven that  $\text{Fe}(\text{CO})_5$  is a nonrigid molecule.<sup>1-5</sup> This fact was initially recognized as a direct result of the unexpectedly simple appearance of the NMR spectrum of  $\text{Fe}(\text{CO})_5$ .<sup>1</sup> Chemical exchange between free  $^{13}\text{C}$  and  $^{18}\text{O}$ , observed with ir spectroscopy,<sup>6</sup> was unmeasurably small. This suggested that the nonrigidity of  $\text{Fe}(\text{CO})_5$  involved an intramolecular exchange mechanism.

From studies of the NMR spectra of polynuclear carbonyls,<sup>7</sup> the activation energy for the transition of a terminal carbon monoxide ligand to a bridging position has proved to be very small. This could imply intermolecular exchange between different  $\text{Fe}(\text{CO})_5$  molecules by a bridging path. In an earlier publication we showed that a CO group bound to a metal atom behaves like an activated CO "molecule".<sup>8</sup> Consequently the exchange experiment to determine whether the mechanism of nonrigidity in  $\text{Fe}(\text{CO})_5$  is intra- or intermolecular should be designed differently than heretofore. The exchange rate should be studied between equally activated carbon monoxide "molecules" in  $\text{Fe}(\text{CO})_5$  rather than between activated and unactivated CO groups as in ref 6.

In the course of our  $^{13}\text{C}$  NMR experiments published elsewhere<sup>5</sup> we observed what must be interpreted as a slow