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IR SPECTROSCOPIC STUDIES ON METAL CARBONYL COMPOUNDS

XXI *. THE SUCCESSFUL APPLICATION OF THE HIGH-ENERGY FACTORED (“NON-RIGOROUS”) FORCE FIELD FOR THE ANALYSIS OF THE IR SPECTRA OF SIX ISOTOPIC SPECIES OF $\text{Co}(\text{CO})_3\text{NO}$

GYÖRGY BOR *

Department of Industrial and Engineering Chemistry, Swiss Federal Institute of Technology ETH, Zurich, CH-8092 (Switzerland)

GIOVANNI BATTISTON and GINO SBRIGNADELLO

Laboratory of the Chemistry and Technology of the Radioelements of CNR, Corso Stati Uniti, Padua, I-35100 (Italy)

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Summary

The high-energy factored model (“Cotton–Kraihanzel type”, non-rigorous force field) is capable of reproducing within $\pm 0.8 \text{ cm}^{-1}$ all the C–O and N–O stretching frequencies of six different isotopic species of $\text{Co}(\text{CO})_3\text{NO}$, if the model is modified by the introduction of “effective atomic masses” which take into account that, in line with Miller’s approach, the quantities dealt with refer to the composite properties of the MCO (or MNO) units. The results obtained by the same method for the isotopically substituted species of $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, and $\text{M}(\text{CO})_6$ [M = Cr, Mo, or W] are also in good agreement with experiment.

Introduction

Jones, McDowell and Swanson [2] reported recently a complete vibrational analysis of the $\text{Co}(\text{CO})_3\text{NO}$ molecule based on the IR spectra of six different isotopic forms. Earlier papers by Jones et al. dealt with similar studies of various isotopic species of $\text{Ni}(\text{CO})_4$ [3], $\text{M}(\text{CO})_6$ (M = Cr, Mo, W) [4], and $\text{Fe}(\text{CO})_5$ [5].

While these studies are extremely valuable from the point of view of fundamental vibrational spectroscopy, it is unlikely that similar studies can be

* For Part XX see ref. 1.

carried out with di- or poly-nuclear and substituted metal carbonyls in the near future. However, chemists working in this field are often interested in force constant data, mainly for isostructural series of carbonyl complexes, because although such data are not rigorous on an absolute scale, they can be obtained in a consistent way by simplified calculations [6].

The most widely used method is that of the high-energy factored C—O stretching force field. The initial publications of Cotton and Kraihanzel [7,8] set out the principles and fundamental relationships for the mononuclear hexacoordinate carbonyl complexes of the type $M(\text{CO})_{6-n}L_n$. Later this method was rendered more flexible and freed of some of its original constraints by the introduction of an independent variable [9–12]. The study of isotopically enriched samples gave additional support to these methods [13–15]. A theoretical analysis of the force and interaction constants, obtained for a high-energy factored model, as composite properties of the M—C—O entities, was given by Miller [16].

In their recent study [2], Jones et al. repeated their earlier criticism [17] of the C—O factored approximation, based on their findings that “a satisfactory solution is impossible to obtain”, since “the best solution ... gives errors greater than 5 cm^{-1} in some of the calculated isotope shifts as compared with the observed values”, and “a closer fit can only be obtained with imaginary force constants”. However, Miller [16] has previously shown that the calculated C—O stretching frequencies of isotopically fully substituted molecules can be expected to be high up to 3 cm^{-1} for $^{13}\text{C}^{16}\text{O}$ and to be low by 4 cm^{-1} for $^{12}\text{C}^{18}\text{O}$ substitution, if obtained in a high-frequency factored model by using the theoretical reduced mass ratios.

In this paper we seek to demonstrate that by the appropriate application of the principles of the C—O factored approximation which involves the use of modified reduced masses, a fit as good as $\pm 0.8 \text{ cm}^{-1}$ or better can be obtained for all the six isotopic species of $\text{Co}(\text{CO})_3\text{NO}$ studied by Jones et al.

Method of calculation

We observed already in an early stage of our studies with isotopically enriched metal carbonyls [18,19] that the “theoretical” values of $(\mu_i/\mu)^{1/2}$ had to be modified to give a good agreement (i.e. within $\pm 0.5 \text{ cm}^{-1}$) between the observed and calculated frequencies of different $L_xM(\text{CO})_{n-1}(*\text{CO})$ molecules (where $*\text{CO} = ^{13}\text{C}^{16}\text{O}$ or $^{12}\text{C}^{18}\text{O}$). These “practical” isotopic mass ratios were found to be lower than the theoretical value for $^{13}\text{C}^{16}\text{O}$ substitution, but were slightly higher than demanded by theory for $^{12}\text{C}^{18}\text{O}$ substituted molecules. This observation has been rationalized [19] in terms of the coupling between the M—C and C—O stretching modes, neglected a priori in the C—O factored model.

In the light of these findings it is straightforward to formulate the quantities of “effective isotopic masses”, m_A (where $A = \text{C}, \text{O},$ or N , in the present case), which show deviations from the true isotopic atomic weights by some 0.01 units, and thus are subject to the uncertainties inherent in the approximations involved in the C—O factored model.

The fundamental considerations and the simple mathematical basis of the practical calculations were given previously [13]. The equations (9) in that

paper should be modified in the following way to allow for the presence of more than one type of isotopic substitution:

$$\text{species } a_1: \begin{cases} y_1 + y_2 = uF_{11} + vF_{22} & (1a) \\ y_1 - y_2 = [(uF_{11} - vF_{22})^2 + 4uvF_{12}^2]^{1/2} & (1b) \end{cases}$$

$$\text{species } e: y_3 = uF_{33} \quad (1c)$$

where $y_i = 0.40407[\nu_i(\text{CO})]^2 \times 10^{-5}$ as in our previous studies [9,13] (ν_1 and ν_2 are identical with the assignments of Jones et al., whereas our ν_3 corresponds to ν_8 of these authors). Further, u refers to the isotopic substitution of the CO ligands and v to that of the NO group affording:

$$u = (m_C^{-1} + m_O^{-1})/(12^{-1} + 16^{-1}) \quad (2a)$$

$$v = (m_N^{-1} + m_O^{-1})/(14^{-1} + 16^{-1}) \quad (2b)$$

The F_{ij} values are obtained, according to our 'independent variable ($\cos \beta$) method' [9,12b] by:

$$\text{species } a_1: \begin{cases} F_{11} = [(y_1 + y_2) + (y_1 - y_2)\cos \beta]/2 & (3a) \\ F_{22} = [(y_1 + y_2) - (y_1 - y_2)\cos \beta]/2 & (3b) \end{cases}$$

$$\text{species } e: F_{33} = y_3 \quad (3c)$$

Here $\cos \beta$ is the parameter reflecting the degree of coupling in species a_1 between the set of the three C—O vibrators and the N—O group. Its value was predicted in our earlier ^{13}CO enrichment study with this compound [13] to lie in the interval 0.96 ... 1.0.

The values of m_C , m_O , and m_N and of $\cos \beta$ were varied by the use of two different computer programs. The optimum was sought by using the least quartics and least squares methods for the differences between experimental and calculated frequencies. The experimental frequencies were taken from Table I of Jones et al.

Results

The final m_A values (± 0.0005) and $\cos \beta$ are: $m_C = 13.0245$; $m_O = 17.8685$, $m_N = 14.9415$, $\cos \beta = 0.965$. The agreement between the experimental frequencies reported by Jones et al. [2] and those calculated by our method is shown in Table 1. Comparison of the $\Delta\nu$ values obtained in this study and those reported by Jones et al. (last two columns in Table 1) reveal in no case a difference greater than 0.7 cm^{-1} . If one keeps in mind the extreme simplicity of our CO-factored approach as compared with a complete vibrational analysis this slightly lower ability to reproduce the measured frequencies should be permissible.

We should like to underline one point. Both the 'complete' vibrational analy-

TABLE 1

EXPERIMENTAL [2] AND CALCULATED $\nu(\text{C-O})$ AND $\nu(\text{N-O})$ STRETCHING FREQUENCIES (cm^{-1}) FOR $\text{Co}({}^{12}\text{C}^{16}\text{O})_3({}^{14}\text{N}^{16}\text{O})$ MOLECULES

<i>i, j, k, l</i>	Found (cald.)			Found — calcd.	
	ν_1	ν_2	ν_3	This work	Jones ^a
12, 16, 14, 16	2108.1 (2108.1)	1822.1 (1822.1)	2046.5 (2046.5)	0.0, 0.0, 0.0	-0.1, -0.1, -0.1
12, 16, 15, 18	2106.8 (2107.0)	1746.0 (1746.3)	2046.5 (2046.5)	-0.2, -0.3, 0.0	-0.1, -0.4, -0.1
12, 18, 14, 16	2062.0 (2061.4)	1821.2 (1821.2)	1999.8 (2000.1)	0.6, 0.0, -0.3	0.0, 0.0, 0.3
12, 18, 15, 18	2060.4 (2059.7)	1746.0 (1745.9)	1999.3 (2000.1)	0.7, 0.1, -0.8	0.0, 0.1, -0.2
13, 16, 14, 16	2060.8 (2061.2)	1821.3 (1821.2)	2000.4 (2000.0)	-0.4, 0.1, 0.4	0.2, 0.0, -0.1
13, 16, 15, 18	2059.1 (2059.6)	1746.2 (1745.9)	2000.5 (2000.0)	-0.5, 0.3, 0.5	0.0, 0.3, 0.1

^a Obtained by the use of a "complete" force field: c.f. Table IX and XI of Ref. 2.

sis and the high-energy factored model give an identical calculated frequency for ν_3 (ν_8 in Jones' notation) of $\text{Co}({}^{12}\text{C}^{18}\text{O})_3({}^{14}\text{N}^{16}\text{O})$ and of $\text{Co}({}^{12}\text{C}^{18}\text{O})_3({}^{15}\text{N}^{18}\text{O})$, whereas the measured frequencies differ by 0.5 cm^{-1} . Hence not even the 'complete' vibrational analysis suffices to account for differences such as this. Evidently this discrepancy in Jones et al.'s study is a result of constraining F_{89} (inter alia) a priori to zero (c.f. Table X in ref. [2]).

TABLE 2

APPLICATION OF THE m_{C} AND m_{O} VALUES (RESULTS SECTION) FOR OTHER METAL CARBONYLS TREATED BY COMPLETE VIBRATIONAL ANALYSES [3-5]: DIFFERENCES BETWEEN OBSERVED ISOTOPIC FREQUENCIES AND THOSE CALCULATED BY THE HIGH-ENERGY FACTORED MODEL

Compound	Ref. ^a	Assign. ^b	$\Delta\nu = \nu_{\text{obs}} - \nu_{\text{calc}} (\text{cm}^{-1})$	
			$\text{M}({}^{13}\text{C}^{16}\text{O})_n$	$\text{M}({}^{12}\text{C}^{18}\text{O})_n$
$\text{Ni}(\text{CO})_4$	3	$\nu_1(a_1)$	-0.8	1.4
		$\nu_5(f_2)$	0.4	-0.8
$\text{Fe}(\text{CO})_5$	5	$\nu_1(a_1')$	-1.2	2.2
		$\nu_2(a_1')$	-0.3	1.8
		$\nu_6(a_2'')$	0.8	-0.5
		$\nu_{10}(e')$	0.2	-0.2
$\text{Cr}(\text{CO})_6$	4	$\nu_1(a_{1g})$	-0.8	1.7
		$\nu_3(e_g)$	-0.2	0.1
		$\nu_6(f_{1u})$	1.0	-1.8
$\text{Mo}(\text{CO})_6$	4	$\nu_1(a_{1g})$	-1.4	2.0
		$\nu_3(e_g)$	0.1	0.0
		$\nu_6(f_{1u})$	1.6	-2.5
$\text{W}(\text{CO})_6$	4	$\nu_1(a_{1g})$	-1.9	2.3
		$\nu_3(e_g)$	-0.3	-0.4
		$\nu_6(f_{1u})$	1.4	-1.9

^a Papers containing the ν_{obs} values. ^b Assignments according to Jones et al. [3-5].

Comments on the m_A values

By using the m_C value obtained as optimum (see Results section) to calculate therefrom $u = (\mu_i/\mu)$ (identical with a of ref. [13] and [18]) we obtain 0.97727 for $^{13}\text{C}^{16}\text{O}$. This is in excellent agreement with the practical value of $a = 0.9774 \pm 0.0002$ obtained previously in the study of partially ^{13}C enriched $\text{Fe}(\text{CO})_5$, and with $\nu_i/\nu = 0.9774$ found for $(\text{Et}_3\text{P})_2\text{Co}(\text{CO})\text{Cl}_2$ [18,19]. Hence the value of $m_C = 13.0245$ can be considered as the generally valid "effective" atomic mass of ^{13}C in isotopic frequency calculations by the high-energy factored model.

The $m_O = 17.8685$ results in a $u = 0.97734$ for the $^{12}\text{C}^{18}\text{O}$ ligand. The previously found ν_i/ν values [19] varied between 0.9769 and 0.9786. More experimental data of high accuracy and precision are needed before a "generally valid" numerical value of m_O for ^{18}O can be suggested.

The value obtained for m_N has only a relative significance, since no "isotopically mixed" NO derivatives were reported by Jones et al. [2]. We used the same m_O value as obtained in the refinement for the carbonyl ligands. With data on $^{14}\text{N}^{18}\text{O}$ and/or $^{15}\text{N}^{16}\text{O}$ derivatives, a different ^{18}O value cannot be excluded for the nitrosyl group, leading to a different m_N . When we allowed our computer program "to float" to search for the optimum without the constraint that the atomic masses of the two types of ^{18}O atoms be equal we obtained $m'_N = 14.9300$ and $m_O^{(\text{NO})} = 17.8870$.

We also used the m_C and m_O values obtained as optima in this study for the other $\text{M}(\text{C}'\text{O})_n$ systems studied by Jones and co-workers. The results are shown in Table 2. In all cases the agreement for $^{13}\text{C}^{16}\text{O}$ substitution is much better than that for $^{12}\text{C}^{18}\text{O}$ substitution. The $\Delta\nu$ differences can be further reduced by changing the m_C value by 0.0025 units for each 0.1 cm^{-1} .

The agreements are not as good for Mo- and W-(CO)₆ as for Cr(CO)₆. This might mean that the high-energy factored model works better for 3d metal carbonyls than their heavier analogues.

Comments on the $\cos \beta$ and valence force constant values

The valence force and interaction constants associated with the 'independent variable' value of $\cos \beta = 0.965$ are: $k(\text{CO})$ 17.24(8); $k(\text{NO})$ 14.66(4); $k(\text{CO}, \text{CO})$ 0.32(5); $k(\text{CO}, \text{NO})$ 0.25(4) (All values are in m dyn/Å. 1 m dyn/Å = 100 N m⁻¹). The earlier prediction [13] for the value of $\cos \beta$, which was based upon a much more limited set of data, but based on the regularities observed for the interaction constants of a high-energy factored force field, is thus confirmed.

On comparing the numerical values of the force and interaction constants with those obtained in the complete vibrational analysis (c.f. Table XII of ref. 2) we find: (i) There is good agreement in the value of $k(\text{CO}, \text{NO})$ and $f(\text{CO}, \text{NO})$ respectively: They are 0.25 m dyn/Å with both methods; (ii) The $f(\text{CO}, \text{CO})$ value of the complete analysis (0.17 m dyn/Å) is only about the half of that obtained in the high-energy factored model; this tendency has been found also for other simple metal carbonyls; (iii) Our $k(\text{CO})$ is lower by 0.41 m dyn/Å and at the same time our $k(\text{NO})$ is higher by 0.89 m dyn/Å than the corresponding f_{ij} values of the complete analysis. The separation between these two values is

thus higher by 1.30 mdyne/Å in the complete vibrational analysis than in a high-energy factored approximation. (The same tendency can be observed concerning the two (axial and equatorial) C—O valence force constants of Fe(CO)₅ [5,18].)

These features are consequences of the different force fields employed. Relationships analogous to those given by Miller [16] for M(CO)₆ complexes, connecting high-energy factored force constants (k_i) characteristic of the MCO units with the "true" valence force constants (f_i) of the C—O bond, can again account for the differences.

In spite of these differences in the nature and hence the numerical values of the force constants (discussion of which is beyond the scope of this paper), the excellent results obtained by this simple method for the isotopic frequencies underlines again the usefulness of the simplified force fields.

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