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Vibrational Modes of Acetylenedicobalt Hexacarbonyl Studied by Neutron Spectroscopy[†]

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The vibrational modes of $(C_2H_2)Co_2(CO)_6$ have been studied by neutron inelastic spectroscopy (NIS) in the energy range 80–2100 cm^{-1}. A reassignment of several vibrations of the C_2H_2 fragment is proposed. The torsion and the hindered rotation of acetylene around the C=C bond are found near 776 cm^{-1}. The torsional mode measuring the potential barrier of C_2H_2 about the axis projected through both the centers of the Co–Co and C=C bonds is assigned at a much higher frequency than in a previous NIS study: 400 cm^{-1} instead of 156 cm^{-1}. This new assignment is supported by calculations of the vibrational frequencies and of the neutron intensities of the whole molecule.

Introduction

The vibrational spectra of molecules adsorbed on transition metals are often assigned by comparing the peak frequencies with the results obtained for model organometallic compounds. For example $K[Pt(C_2H_4)Cl_3]$ (Zeise's salt) and $(C_6H_6)Cr(CO)_3$ have been used to assign the vibrational spectra of ethylene or benzene adsorbed on metal surfaces.[1-7] In the case of acetylene adsorbed on platinum black, the neutron vibrational data were interpreted by using acetylenedicobalt hexacarbonyl, $(C_2H_2)Co_2(CO)_6$, as a model.[8] No solid-state structure of this complex has been reported, but the geometry is very close to that for $(Ph_2C_2)Co_2(CO)_6$[9] or $(t\text{-}Bu_2C_2)Co_2(CO)_6$.[10] In these complexes, the acetylene moiety is bonded perpendicular to the Co–Co bond. The C_{ac}–C_{ac} bond length has values in the range 1.3–1.4 Å, and this lengthening can be understood in terms of the Dewar–Chatt–Duncanson model.[11] There is σ donation from the filled π orbitals of acetylene to empty $Co_2(CO)_6$ orbitals and back-donation from filled orbitals of the dimetal fragment to the empty π^* orbitals of acetylene.

Hoffman et al.[12] have performed a molecular orbital analysis of $(C_2H_2)Co_2(CO)_6$ (Figure 1) by assuming the following structural parameters: Co–Co = 2.46 Å, C_{ac}–C_{ac} = 1.32 Å, Co–C_{ac} = 2 Å, and ∠C–C–H = 130°. They calculated a correlation diagram for the rotation from perpendicular (Figure 1) to parallel orientation. They found that the parallel orientation was 2.5 eV above the perpendicular one in energy.

The infrared and Raman spectra of this complex have been reported.[13,14] A C_{2v} symmetry for the coordinated acetylene was derived from infrared and NMR studies of $(C_2H_2)Co_2(CO)_6$ and of some isotope-substituted molecules.[13] An approximate normal-coordinate treatment of the $(C_2H_2)Co_2$ fragment was performed by Iwashita.[15] More recently, neutron inelastic scattering (NIS) has been used to study the vibrational modes of the $(C_2H_2)Co_2(CO)_6$ molecule,[16] but the assignment of several vibrational modes is still unclear.

We report in this paper a new measurement of the NIS spectrum of $(C_2H_2)Co_2(CO)_6$, in the energy range 80–2100 cm^{-1}. Compared to the previous NIS study,[16] the energy range has been extended and the resolution has been improved, especially at high-energy transfers. The vibrational frequencies have been calculated from a normal-coordinate analysis of the whole molecule. However we are mainly concerned with the vibrations involving acetylene because they correspond to the largest features in the NIS spectrum. The CO stretching and Co–CO stretching and bending vibrations cannot be characterized with NIS because they have weak intensities. A reassignment of several vibrations of the acetylene moiety is presented.

Experimental Section

The NIS spectrum was obtained by using the beryllium-filter detector spectrometer INFB, at the Institut Laue-Langevin, Grenoble, France. The energy range 10–260 meV was covered with the (200), (220), and (331) reflections of a copper monochromator (1 meV = 8.065 cm^{-1}). Details on this spectrometer are given elsewhere.[17] The vibrational peaks in the raw data are shifted up in energy by ≈32 cm^{-1}, because of the beryllium-filter transmission function. The spectra and frequencies given in this paper have however been corrected for this effect. The estimated absolute accuracy is of ±15 cm^{-1}.

Below 800 cm^{-1}, the instrumental resolution is dominated by the band-pass of the beryllium filter (the fwhm is ≈30 cm^{-1}). At higher energy transfers, the resolution is limited by the mosaic spread of the monochromator and by the collimation; in this range $\Delta E/E_0$ is of the order of 5%.

The compound $(C_2H_2)Co_2(CO)_6$ was prepared according to the method described in ref 13: $Co_2(CO)_8$ is dissolved in *n*-pentane, and C_2H_2 is admitted to the solution at 0 °C under argon atmosphere. The reaction mixture was chromatographed on silica, and the complex was distilled under vacuum. The sample was transferred to a thin-walled aluminum container and cooled to 5 K by using a standard liquid-helium cryostat. Such a low temperature is required in NIS to sharpen the fundamentals by decreasing the effect of the Debye–Waller factor.[17]

Results

The NIS spectrum of $(C_2H_2)Co_2(CO)_6$, obtained at 5 K between 80 and 2100 cm^{-1}, is shown in Figure 2a. The data were not corrected from the scattering of the empty aluminium container; this produces weak bands at 206 and 314 cm^{-1}. The CH stretching region, above 3000 cm^{-1}, was not investigated because of the broad instrumental resolution and of the multiphonon contributions in that energy range. Our experimental results are in agreement with the previous NIS study,[16] but the energy resolution has been improved and we have extended the frequency range at high-energy transfers.

In neutron scattering, the hydrogen atom has a very large incoherent cross section, σ_H; therefore, the intensity scattered by the sample will be dominated by vibrational motions of the hydrogen atoms.[18] In neutron energy loss, the double-differential cross section for a fundamental vibration is given by[17]

$$\frac{d^2\sigma}{d\Omega dE} = \frac{k'}{k_0}\frac{\sigma_H}{4\pi}\sum_d \exp(-2W_d)\frac{\hbar|Q\cdot C_d^\lambda|^2}{2m_d\omega_\lambda}\delta(\hbar\omega - \hbar\omega_\lambda) \quad (1)$$

The neutron momentum transfer, $\hbar Q$, is defined by $Q = k_0 -$

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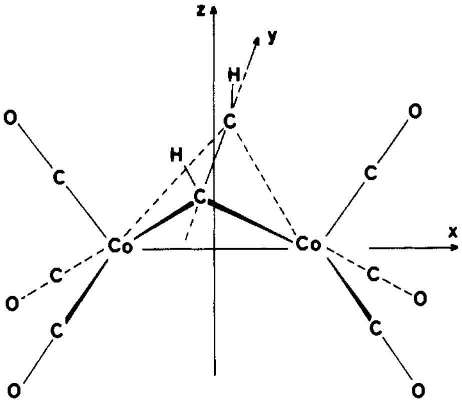

Figure 1. Structure of $(C_2H_2)Co_2(CO)_6$.

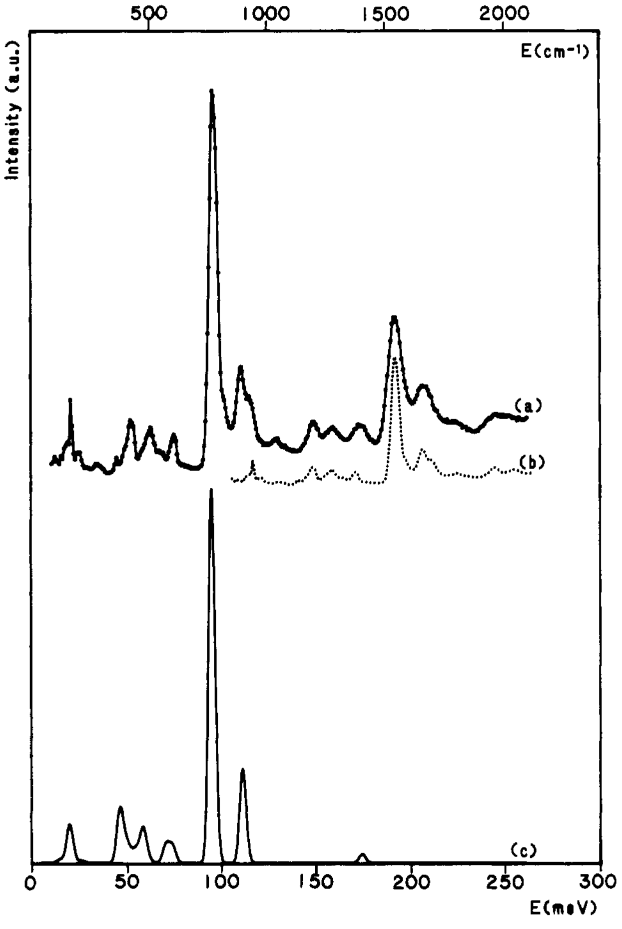

Figure 2. (a) Experimental neutron spectrum, obtained at 5 K, of $(C_2H_2)Co_2(CO)_6$. (b) Spectrum corresponding to the data ranging from 80 to 1350 cm^{-1}, shifted up in energy by 776 cm^{-1} and reduced by a factor 3. (c) Neutron spectrum calculated by using only the intensities of the fundamentals.

k', where k_0 and k' are respectively the incident and final wave vectors. The influence of the Debye–Waller factor for an atom d, $\exp(-2W_d)$, is minimized when the spectra are recorded at low temperature.[17]

Therefore, in the one-phonon approximation, one obtains peaks at frequencies ω_λ corresponding to the normal modes λ. The intensities of the transitions are governed by the vectors C_d^λ, which are the mass-weighted eigenvectors of the normal modes λ (these vectors can be derived from a force field calculation[19]).

Because of its large incoherent cross section, the modes involving the hydrogen atoms will give rise to the largest features in NIS.[17] Further, those leading to the largest hydrogen displacements will be the most intense; e.g. in $(C_2H_2)Co_2(CO)_6$, the in-plane and out-of-plane CH bending modes are expected to yield the largest intensities.

Conversely, the vibrations that involve the CO groups will have weak NIS intensity, e.g. the CO stretching modes around 2000 cm^{-1}.

However, overtones and combinations bands can also be found in the NIS spectra; for example, the intensity of a first overtone will be proportional to

$$\left[\frac{\hbar|Q\cdot C_d^\lambda|^2}{2m_d\omega_\lambda}\right]^2$$

This term is not negligible when C is large. Such is the case in $(C_2H_2)Co_2(CO)_6$ because of the large intensity of the band situated at 776 cm^{-1} in Figure 2a. Its first overtone is found at 1540 cm^{-1}, and above 900 cm^{-1} combinations with the other modes are detected. To put this in evidence, the NIS spectrum ranging from 80 to 1350 cm^{-1} has been shifted up by 776 cm^{-1} and reduced by a factor 3 in Figure 2b (dotted line). This shows that almost all the features measured between 900 and 2100 cm^{-1} do not correspond to fundamentals. Their intensities were not calculated in this work because of the large number of modes that should be taken into account.

Table I. Force Field for $(C_2H_2)Co_2(CO)_6$[a]

force const	notation	value
ν(C–C)	R	6.97
ν(C–H)	r	5.25
$\nu(Co–C_{ac})$	S	1.49
ν(Co–Co)	m	0.87
ν(Co–CO)	t	2.62
ν(C–O)	u	16
δ(OC–Co–CO)	β	0.3
$\delta(OC–Co–C_{ac})$	γ	0.31
δ(H–C–Co)	ψ	0.22
δ(H–C–C)	δ	0.29
δ(Co–Co–CO)	α	0.2
δ(Co–C–O) in plane	$\delta_{CO\parallel}$	0.49
δ(Co–C–O) out of plane	$\delta_{CO\perp}$	0.52
ν(C–O)/ν(C–O)	uu	0.3

[a] The valence force constants are in mdyn Å^{-1}, and the deformations, in mdyn Å rad^{-2}.

Force Field Determination. The normal modes frequencies, ω_λ, and the displacement vectors, C_d^λ, were derived from a force field calculation by using the **G F** matrix method.[19]

The geometry of the molecule was based on the following structural parameters:[15] d(C–C) = 1.388 Å, d(C–H) = 1.08 Å, d(Co–Co) = 2.47 Å, and $d(Co–C_{ac})$ = 2.0 Å. The angle CCH was taken as 140°, because for this value one obtains the correct splitting of the symmetric and antisymmetric CH bending modes. The bond lengths and bond angles for the carbonyls were taken from the X-ray study of Sly.[9]

The initial force constants were taken from the work of Bor[20] for the C–O stretching and interaction constants and from Zeise's salt[5] and the previous normal-coordinate treatment[15] of $(C_2H_2)Co_2(CO)_6$ for the metal–acetylene fragment.

The final force field is shown in Table I; it contains 14 force constants. Force constants for the CH and CO stretches have been included for completeness, but they were not refined, since no new information has been obtained for these modes from NIS.

Assuming that $(C_2H_2)Co_2(CO)_6$ has C_{2v} symmetry, one expects 48 fundamental vibrations. All the frequencies calculated from the force field are not listed in Table II; only those which have some NIS intensity have been considered. The CO stretches have been well characterized by Raman spectroscopy,[14] and since several stretching or deformation modes of the $Co_2(CO)_6$ fragment do not mix with acetylene, they have therefore a negligible NIS intensity and they were not included in Table II.

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Table II. Comparison of Vibrational Frequencies (in cm^{-1}) of $(C_2H_2)Co_2(CO)_6$ Obtained from Experiment (IR, Raman, NIS) with Those Calculated from Normal-Coordinate Analysis Along with Their Symmetry, Potential Energy Distribution (PED), NIS Intensity, and Approximate Description

obsd freq	calcd freq	sym	PED	NIS intens	description
3116[a]	3117	A_1	r(98)	0.895	ν_s(CH)
3086[a]	3099	B_2	r(100)	0.918	ν_{as}(CH)
1403[a,c]	1404	A_1	R(92)	0.081	ν(CC)
894[a,c]	894	B_2	$\delta(77)$, $\psi(15)$	0.636	δ_{as}(CH)
776[c]	790	B_1	$\psi(90)$	0.724	rotation/C=C(R_y)
776[c]	784	A_2	$\psi(94)$	0.765	torsion (C_2H_2)
768[a,c]	766	A_1	$\delta(69)$, $\psi(20)$	0.846	δ_s(CH)
610[a,c,d]	595	A_1	S(38), t(33)	0.092	$t_z + \nu$(Co–CO)
565[c]	573	B_1	t(49), S(21)	0.057	ν(Co–CO) + t_x
550[a,c,d]	563	B_2	t(45), S(22)	0.051	ν(Co–CO) + R_x
510[b,c]	495	A_1	$\delta_{CO\parallel}(39)$, t(20)	0.017	δ(CO) + ν(Co–CO)
	472	B_2	S(55), $\delta_{CO\perp}(17)$	0.179	$R_x + \delta$(CO)
	446	B_2	$\delta_{CO\parallel}(49)$, $\delta_{CO\perp}(25)$	0.011	δ(CO)
	444	B_1	$\delta_{CO\perp}(38)$, $\delta_{CO\parallel}(33)$	0.037	δ(CO)
	443	A_1	$\delta_{CO\parallel}(65)$, $\delta_{CO\perp}(15)$	0.011	δ(CO)
	424	A_1	t(39), S(22)	0.032	ν(Co–CO) + t_z
430[b,c]	403	B_1	t(55), S(25)	0.071	ν(Co–CO) + t_x
	383	B_1	t(62), S(30)	0.079	ν(Co–CO) + t_x
	374	A_2	S(80)	0.211	R_z
210[a,d]	210	A_1	m(79)	0.01	ν(CoCo)
165[c]	163	B_2	$\gamma(88)$	0.167	t_y
	122	B_1	$\gamma(45)$, $\alpha(18)$, $\beta(17)$	0.016	deformation

[a] Reference 13. [b] Broad. [c] This work. [d] Reference 14.

One of the main characteristics of NIS is that both the frequencies *and* the intensities can be computed from a force field. For the simulation of the NIS spectrum of $(C_2H_2)Co_2(CO)_6$ (Fig 2c), only the intensities from the fundamentals were calculated. The influence of the Debye–Waller factor was neglected; this is justified by the small hydrogen mean-square amplitude and by the low temperature used to record the NIS spectrum. Comparison with Figure 2a shows that the experimental intensities of the fundamentals are correctly reproduced but that some frequency shifts occur for the modes situated between 300 and 700 cm^{-1}.

Discussion

It appears from Table II that the internal modes of acetylene are well-defined, but the modes of acetylene relative to the $Co_2(CO)_6$ fragment are more difficult to locate due to mixing; e.g., the mode at 511 cm^{-1} previously assigned[16] to R_x (or τ_x) is found to correspond to δ(CO) and to the Co–CO stretch.

The CC stretching mode is calculated at 1404 cm^{-1}, in agreement with previous infrared work.[15] The NIS intensity calculated for this mode is relatively weak, but nevertheless it makes a contribution to the NIS spectrum at the correct frequency. The CC stretching force constant has been much reduced compared to the gas-phase value ($\approx$16 mdyn Å^{-1}), which indicates a strong interaction between acetylene and the dimetal fragment. The calculated force constant of 6.97 mdyn Å^{-1} is almost the same as the one derived for Zeise's salt,[5] and it gives a bond order value (n) close to 1.6.

Within instrumental resolution, three modes appear as accidentally degenerate and yield the largest peak at 776 cm^{-1}. These are the symmetric CH deformation, δ_s(CH), of A_1 symmetry, the torsion of acetylene (A_2), and the hindered rotation of C_2H_2 around the C=C bond (B_1). The antisymmetric CH deformation, δ_{as}(CH), of B_2 symmetry is found at 894 cm^{-1}. This is in agreement with infrared work[15] but not with the previous NIS study,[16] where this mode was located at 618 cm^{-1}. The assignment of δ_s(CH) at 770 cm^{-1} also differs from the previous NIS work, where it was situated at 903 cm^{-1}; on the other hand, it corresponds to the original infrared assignment of Iwashita.[15] Compared to infrared results, the extra information gained from the NIS intensities is the location of the B_1 and A_2 modes at $\approx$776 cm^{-1}; this assignment is in agreement with the previous NIS study,[16] where the torsion (A_2) of the nonlinear acetylene molecule was called δ_{as}(C–H).

The assignment of the lower frequency modes is more difficult. The force field calculation shows that it is impossible to make an assignment simply in terms of translations or rotations of the whole C_2H_2 molecule. For example, the symmetric and antisymmetric Co–C_2H_2 stretches (t_z and R_x) cannot be unequivocally assigned to particular bands.

The torsional mode of C_2H_2 about the axis projected through both the centers of the Co–Co and C_{ac}–C_{ac} bonds, $R_z(A_2)$, has been previously assigned by NIS[16] at 156 cm^{-1}. However, in Zeise's salt, where the interaction energy with the metal is weaker, this torsional mode was found at 185 cm^{-1} by NIS.[21] Therefore we think that this mode should be found at a higher frequency in $(C_2H_2)Co_2(CO)_6$. Our force field calculation indicates that the band observed by NIS at 165 cm^{-1} can be assigned to $t_y(B_2)$ whereas the mode R_z is calculated at a much higher frequency: 374 cm^{-1}. The reverse assignment was tested, but it was not possible to fit the frequencies, even by adding additional interaction force constants. Experimentally a peak is found at 430 cm^{-1}, but it is made of several modes and thus only an approximate frequency of 400 cm^{-1} can be proposed for this torsional mode. Since the potential function $V(\phi)$ is not known for this molecule, it is difficult to derive the potential barrier to rotation of C_2H_2 from the torsional frequency. If one takes the simplest model for the potential function: $V(\phi) = (V_2/2)(1 - \cos 2\phi)$ as in ref 16, the value calculated for the barrier height, using the harmonic approximation, is 4.3 eV. This is much higher than the value derived from the previous NIS study[16] of 0.65 eV, but it is closer to the results of Hoffman et al.,[12] since a frequency of 305 cm^{-1} is derived from the theoretical barrier: 2.5 eV.

Conclusion

Neutron inelastic spectroscopy is very efficient for locating vibrational modes of hydrogenated molecules. In the case of $(C_2H_2)Co_2(CO)_6$, the torsion and the hindered rotation of C_2H_2 around the C=C bond have been situated near 776 cm^{-1}. The modes of C_2H_2 relative to $Co_2(CO)_6$ have been more difficult to assign due to mixing. The torsional mode of C_2H_2 relative to the axis projected through both the centers of the Co–Co and C=C bonds has however been assigned near 400 cm^{-1}; this yields a potential barrier to rotation much higher than previously proposed.

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