Incoherent Inelastic Neutron Spectra of Hydridocarbonyls. Mid-infrared Vibrational Frequencies for $HCo(CO)_4$

By J. W. WHITE* and C. J. WRIGHT

(*Physical Chemistry Laboratory, South Parks Road, Oxford* OX1 3QZ)

Summary The mid-i.r. vibration frequencies for $HCo(CO)_4$ have been identified by combining i.r. and neutron-scattering spectroscopy.

IN incoherent inelastic neutron scattering spectroscopy (I.I.N.S.S.) a beam of monoenergetic neutrons is scattered from a compound in a way similar to the Raman scattering of light.[1] The vibrational energy levels of the scatterer can be determined from the energy shifts of scattered neutrons. Two important differences are that the scattering is predominantly from hydrogen atoms if these are present and that the intensity of scattering is proportional to the square of the amplitude of the hydrogen motion in the system.

The vibrational spectra of metal carbonyls have been the subject of numerous practical and theoretical investigations.[2] By examining $HCo(CO)_4$ with a neutron spectrometer it has been possible to make new assignments for all the mid-i.r. bands and so to draw comparisons with other compounds *e.g.* $Ni(CO)_4$. Although neutron spectroscopy has no electromagnetic selection rules inhibiting molecular excitation, the neutron spectrum here contains fewer strong bands than the i.r. spectrum. This is an example of an exclusion rule which may be valuable for making assignments in other molecules, namely, that the vibration must be of such a symmetry as to cause hydrogen atom displacements.

$HCo(CO)_4$ and $HCo(PF_3)_4$ were enclosed in aluminium containers and cooled to — 185°. The neutron spectrometer used was the PLUTO triple-axis machine with a beryllium filter detector[3] at Harwell U.K. Neutrons are energy-selected by scattering from a single crystal and passed through a Soller-slit collimator on to the specimen. Neutrons scattered by the specimen are energy-filtered by a liquid-nitrogen-cooled beryllium polycrystal before detection. This filter only passes neutrons whose energies

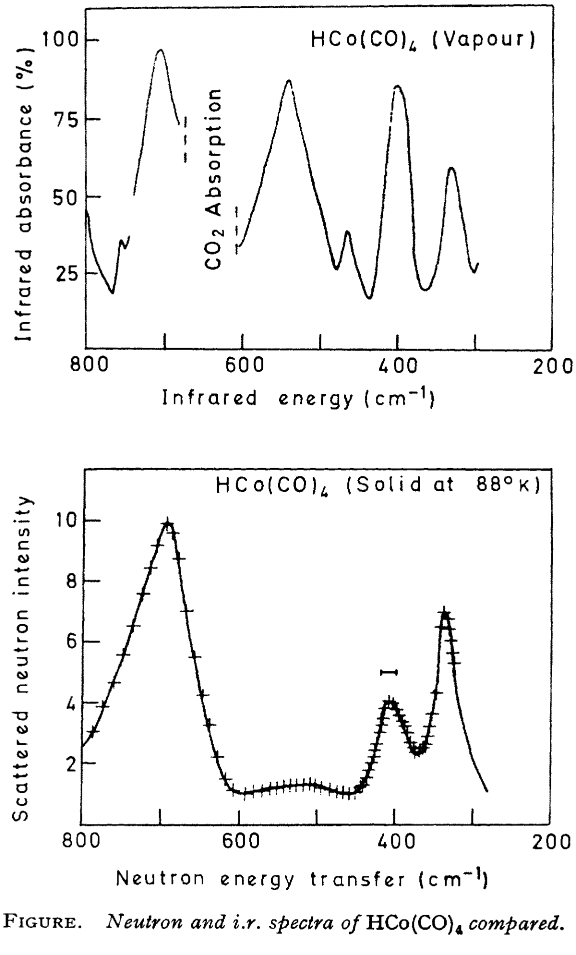

FIGURE. *Neutron and i.r. spectra of* $HCo(CO)_4$ *compared.*

after scattering are less than 42 cm^{-1}. The width of this "window" means that when the energy of the monochromatic incident neutrons is greater than 300 cm^{-1} the energy resolution, $\Delta E/E$, of the detected beam becomes small in comparison with the energy transfer (E).

The spectra were taken from 300—1400 cm^{-1} where the incident neutron intensity becomes too low to obtain statistically good results. The Figure shows the neutron and i.r. spectra compared.

The bending symmetry-co-ordinate of the hydrogen atom is of E symmetry, so that the other E vibrations of $HCo(CO)_4$ will to a greater or lesser extent involve hydrogen motion by mixing, and have intensity in the I.I.N.S. spectrum. The corollary is that A_1 vibrations will have i.r. but no I.I.N.S. intensity. Using this argument the band at 468 cm^{-1}[4] is assigned as the A_1 Co–C stretch.

The band at 703 cm^{-1} is intense in the i.r. spectrum. This would not be so if the band involved only the hydrogen bond with its low electron density.[5,6] That the hydrogen bending mode occurs in this region is shown by the I.I.N.S. spectrum of $HCo(PF_3)_4$ where again a very strong mode occurs at 640 cm^{-1}. Here the H bending mode interacts mainly with P–F stretches. From this one deduces that the E symmetry hydrogen bend and the E and A (from F_2 in T_d) carbonyl bending motions both occur at about 700 cm^{-1}.

The I.I.N.S. active band at 530 cm^{-1} is the E (from F_2 in T_d) Co–C stretching vibration which changes only slightly from $Co(CO)_4$ to $HFe(CO)_4^-$. The two remaining vibrations at 403 and 331 cm^{-1} must be analogues of the elusive vibrations of $Ni(CO)_4$ at 380 and 303 cm^{-1} and are consequently assigned as the E (from E in T_d) and the E (from F_1 in T_d) vibrations, respectively.

The mid-i.r. E vibration of $Ni(CO)_4$ was considered by Jones[7] to be undetermined although some evidence[8] has been obtained placing it at 380 cm^{-1} with the A_1 vibration. In $HCo(CO)_4$ this vibration occurs at 403 cm^{-1}.

The spectra (Figure) and assignments from them accommodate $HCo(CO)_4$ more satisfactorily in a correlation scheme than previous attempts.[4,7,9,10] They also produce evidence for assigning the mid-i.r. E vibration of $Ni(CO)_4$.

We thank Dr. A. J. Deeming, Dr. C. E. Holloway, Dr. B. F. G. Johnson, and Professor J. Lewis of the Chemistry Department, University College, London, for providing us with the compounds $HCo(CO)_4$ and $HCo(PF_3)_4$.

(*Received, May 20th,* 1970; *Com.* 783.)

[1] P. A. Reynolds and J. W. White, *Discuss. Faraday Soc.*, 1969, **48**, 131.

[2] D. M. Adams, "Metal–Ligand and Related Vibrations," Arnold, London, 1967.

[3] M. F. Collins, B. C. Haywood, and R. D. Lowde, *J. Sci. Instr.*, to be published, and B. C. Haywood, *Discuss. Faraday Soc.*, 1969, **48**, 163.

[4] W. F. Edgell, C. Magee, and G. Gallupp, *J. Amer. Chem. Soc.*, 1956, **78**, 4185.

[5] D. K. Huggins, W. Fellman, J. M. Smith, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1964, **86**, 4844.

[6] W. F. Edgell and R. Summitt, *J. Amer. Chem. Soc.*, 1961, **83**, 1772.

[7] L. H. Jones, *Spectrochim. Acta*, 1963, **19**, 1899.

[8] G. Bouquet, A. Loutellier, and M. Birgogne, *J. Mol. Structure*, 1967, **1**, 2111.

[9] H. Stammreich, K. Kawai, Y. Tavares, P. Krumholz, J. Behmoiras, and S. Bril, *J. Chem. Phys.*, 1960, **32**, 1452.

[10] W. F. Edgell, W. E. Wilson, R. Summitt, and W. C. Nieuwpoort, U.S. Atomic Energy Commission, 1961, TID-15242.