Incoherent Inelastic Neutron Spectra of Hydridocarbonyls. Mid-infrared Hydrogen Vibrations of $H_3Mn(CO)_{12}$

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Summary The incoherent inelastic neutron spectrum (I.I.N.S.) of $H_3Mn_3(CO)_{12}$ shows the mid-i.r. hydrogen vibrations of the molecule unobscured by other bands.

THE conventional approach of detecting i.r. and Raman spectral changes on deuteriation to confirm the presence of hydrogen in hydridocarbonyls is often very difficult,[1-3] and in the case of $H_3Re_3(CO)_{12}$ there is indeed no correspondence between the shifts observed by the two methods [Figure (a) and (c)]. Assignment of the hydrogen modes is difficult in optical spectroscopy because these vibrations fall in regions of the spectrum where there are other modes of greater intensity. Because of the different selection rules for neutron scattering spectroscopy, hydrogen modes appear strongly. The spectrum of $H_3Mn_3(CO)_{12}$ shows how readily I.I.N.S. spectroscopy can be used to determine the frequencies of vibrations involving hydrogen atoms.

The search for a metal–hydrogen vibration in the Raman spectrum of $H_3Re_3(CO)_{12}$[3] was only partially successful. Only a very weak and very broad band was observed at 1100 cm^{-1} which shifted to 787 cm^{-1} on deuteriation. In the i.r. spectrum,[2] a shoulder at 625 cm^{-1} (B) (Figure) disappeared under a band at 588 cm^{-1} on deuteriation, whilst a band at 339 cm^{-1} (A) (Figure) disappeared beyond the range of the scan. These changes although subtle were "reproducible and reversible," but the overwhelming contributions to the spectrum from other motions is clear.

Frequencies of bands in the I.I.N.S. spectrum of $H_3Mn_3(CO)_{12}$

$H_3Mn_3(CO)_{12}$ I.I.N.S.	$H_3Re_3(CO)_{12}$[2] I.r.
608 ± 6·5 cm^{-1}	625 cm^{-1}
312 ± 1·8 cm^{-1}	339 cm^{-1}

In the Figure (b) the I.I.N.S. spectrum of $H_3Mn_3(CO)_{12}$,† is compared with the published i.r. 1(a); and Raman 1(c) spectra of $H_3Re_3(CO)_{12}$. The difficulties of using the Raman spectrum are apparent since only the weak band, C, could be associated with the hydrogen motions. By contrast, in the neutron spectrum the observed modes may be assigned to the hydrogen vibrations since, on the basis of scattering cross-sections alone, the ratio of hydrogen

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scattering to the rest is 2 : 1. The intensity of scattering is also proportional to the square of the atomic vibrational amplitude (*i.e.* approximately to $1/M$ where M is the mass of the vibrating atom). For these compounds this ensures an extra relative intensity factor of 12×.

The frequencies are close to those observed in the rhenium compound and confirm the assignments by analogy (Table).

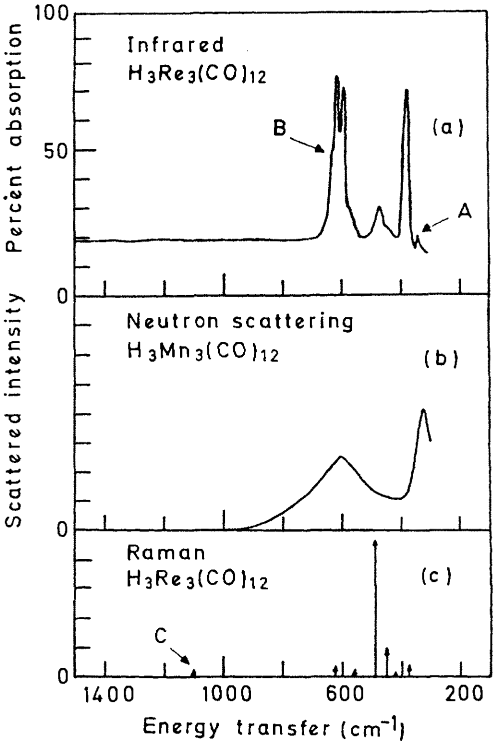

FIGURE. *Comparison of mid-i.r. spectrum* (*Ref.* 2) (a) *and Raman spectrum* (*Ref.* 3) (c) *of* $H_3Re_3(CO)_{12}$ *with the I.I.N.S. spectrum of* $H_3Mn_3(CO)_{12}$ (b); A, B, C *shift on deuteriation*; C *very weak and broad.*

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[1] Preceding communication.

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

[3] J. M. Smith, W. Fellman, and L. M. Jones, *Inorg. Chem.*, **1965**, **4**, 1361.