# Mössbauer Study of the Dynamic Behaviour of Gold in Molecular Crystals

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Measurements are reported of the temperature dependence of the Mössbauer fraction of a number of $Au^{I}$ and $Au^{III}$ complexes. A simple model is described with which this temperature dependence of the Mössbauer fraction was analysed in terms of intra- and inter-molecular vibrations. The observed difference between Mössbauer fractions of $Au^{I}$ and $Au^{III}$ complexes has to be attributed mainly to the larger mass of the latter, rather than to the difference in co-ordination number.

THE crystals of most gold compounds are built up from molecules. The dynamic behaviour of atoms in such systems of generally low symmetry is quite complicated. Some aspects of it may be clarified by the Mössbauer effect, which probes the mean-square displacement $\langle x^2 \rangle$ of one particular kind of atom (the Mössbauer nucleus) in the lattice. The value of $\langle x^2 \rangle$ is obtained from the Mössbauer fraction $f$, and $f$ can be determined from the relative absorption intensity of the lines in the spectrum.

Our interest in this subject stemmed from the observation that, in the mixed-valence gold compounds studied by us the relative absorption intensity of the square-planar four-co-ordinated gold(III) site is about twice that of the linear two-co-ordinate gold(I) site, whereas we found, in a compound containing two four-co-ordinated gold(III) sites, approximately equal intensities for both sites. This is illustrated in Figure 1 and Table 1. A correlation between the Mössbauer fraction and the co-ordination number of the gold atom seemed a possible explanation: a two-co-ordinated atom might have a larger vibrational amplitude than a four-co-ordinate one. However, the intramolecular binding forces are typically two orders of magnitude larger than the intermolecular (van de Waals) forces and molecular crystals can therefore be thought of as constructed from rigid molecules, which vibrate as a whole. This is a rather generally held viewpoint, strongly advocated in the work of Herber *et al.*[1-3] Nevertheless, the intramolecular vibrations cannot be neglected. The arguments, used by Kagan and Iosilevskii [4] for impurities in a crystal, may be applied here: for the $3N$ ($N$ = number of molecules in the lattice) intermolecular vibrational modes the energy assignable to a single molecule is of the order of $1/N$ of that of each mode. On the other hand, a considerable part of the energy of localized intramolecular vibrations, although few in number, is associated with the motion of the Mössbauer nucleus. Thus the contribution of inter- and intra-molecular vibrations to $\langle x^2 \rangle$ can be expected to be of the same order of magnitude.

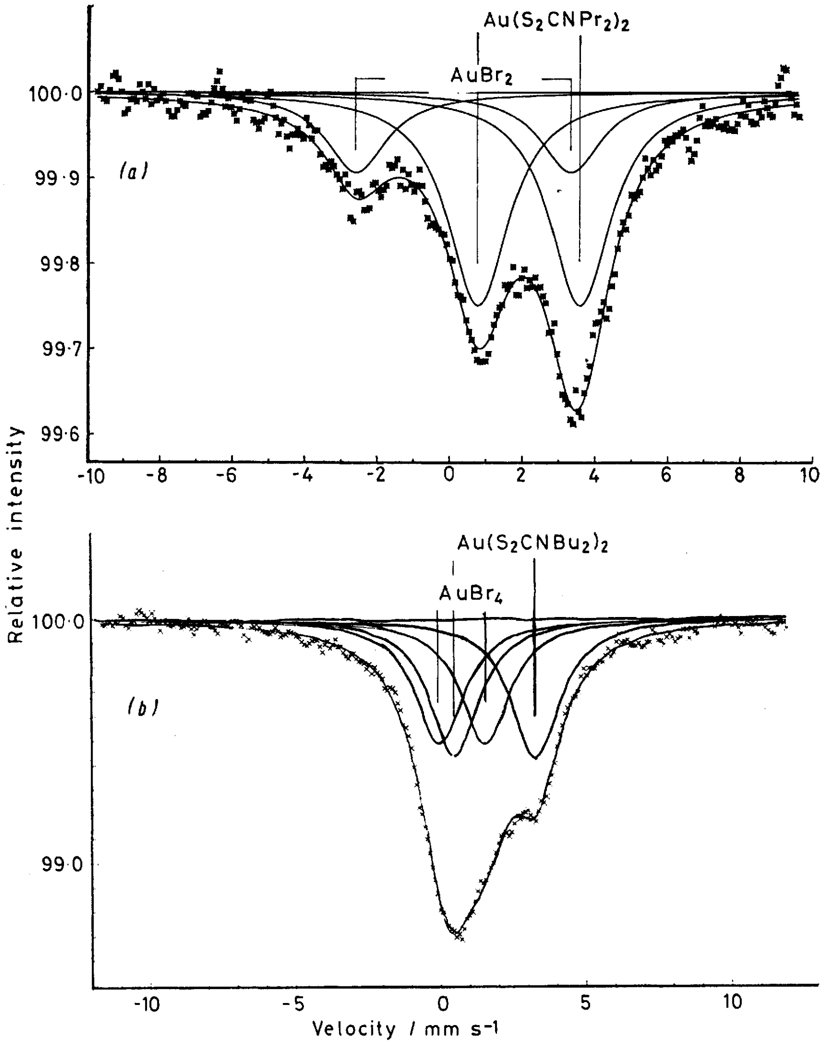

FIGURE 1 Mössbauer spectra of (*a*) $[\mathrm{Au^{III}(S_2CNPr_2)_2}][\mathrm{Au^{I}Br_2}]$ and (*b*) $[\mathrm{Au^{III}(S_2CNBu_2)_2}][\mathrm{Au^{III}Br_4}]$. The full line connecting the points is a least-squares fit with two pairs of Lorentzian-shaped absorption lines. The lines of each pair were constrained to have equal intensities and widths

In order to determine the characteristic frequencies of the inter- and intra-molecular vibrations from the temperature dependence of the Mössbauer fraction we developed a simple model which is presented in the next section. (Dibenzyl sulphide)dihalogenogold compounds present a suitable test case. They consist of

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[1] Y. Hazony and R. H. Herber, 'Mössbauer Effect Methodolody,' 1973, vol. 8.

[2] Y. Hazony and R. H. Herber, *J. de Physique, Coll.*, 1974, **35**, C6—131.

[3] A. J. Rein and R. H. Herber, *J. Chem. Phys.*, 1975, **63**, 1021.

[4] Yu. Kagan and Ya. A. Iosilevskii, *Soviet Phys. JEPT*, **1962**, **15**, 182.

separate molecules of $[Au^{I}X\{S(CH_2Ph)_2\}]$ and $[Au^{III}X_3\{S(CH_2Ph)_2\}]$ (X = Br or Cl) packed in rows in which alternating gold atoms have oxidation states of I and III.[5] As usual, the gold(I) site has linear two-co-ordination and the gold(III) site has planar four-co-ordination. Moreover, the mono- and tri-valent species can be studied in pure form. The results of our measurements on these compounds as well as some other compounds are discussed.

TABLE 1

Mössbauer data for mixed-valence gold compounds at 4.2 K

| Compound | Ref.[a] | Quadrupole splitting (q.s.) mm s$^{-1}$ | Isomer shift (i.s.) mm s$^{-1}$ | Intensity ratio[b] ($Au^{III}$ : $Au^{I}$) |
|---|---|---|---|---|
| $[Au(S_2CNBu_2)_2][AuCl_2]$ | *c* | $6.43 \pm 0.08$ | $0.74 \pm 0.05$ | 3.3 |
| | | $2.75 \pm 0.08$ | $2.00 \pm 0.05$ | |
| $[Au(S_2CNBu_2)_2][AuI_2]$ | *c* | $5.75 \pm 0.08$ | $0.53 \pm 0.05$ | 2.2 |
| | | $2.76 \pm 0.08$ | $2.00 \pm 0.05$ | |
| $[Au(S_2CNPr_2)_2][AuBr_2]$ | *d* | $6.2 \pm 0.3$ | $0.4 \pm 0.1$ | 2.6 |
| | | $2.7 \pm 0.1$ | $2.0 \pm 0.1$ | |
| $[Au(S_2CNPh_2)_2][AuBr_2]$ | *d* | $6.5 \pm 0.2$ | $0.5 \pm 0.1$ | 4.0 |
| | | $2.29 \pm 0.03$ | $1.83 \pm 0.3$ | |
| $[AuCl\{S(CH_2Ph)_2\}]$, | 5 | $6.35 \pm 0.2$ | $1.05 \pm 0.1$ | 2.0 |
| $[AuCl_3\{S(CH_2Ph)_2\}]$ | | $2.16 \pm 0.02$ | $1.38 \pm 0.01$ | |
| $[AuBr\{S(CH_2Ph)_2\}]$, | 5 | $5.92 \pm 0.03$ | $0.57 \pm 0.02$ | 2.0 |
| $[AuBr_3\{S(CH_2Ph)_2\}]$ | | $1.93 \pm 0.03$ | $0.94 \pm 0.02$ | |
| $[Au(S_2CNBu_2)_2][AuBr_4]$ | *d* | $1.53 \pm 0.08$ | $0.91 \pm 0.05$ | 1.2[e] |
| | | $2.81 \pm 0.08$ | $2.04 \pm 0.05$ | |

[a] For preparation and structure. [b] Area ratio of the least-squares-fitted Lorentzians. [c] P. T. Beurskens, H. J. A. Blaauw, J. A. Cras, and J. J. Steggerda, *Inorg. Chem.*, 1968, **7**, 805. [d] J. G. M. van der Linden, *Rec. Trav. chim.*, 1971, **90**, 1027. [e] Area ratio of cation : anion.

## THEORY

If the vibration amplitude of a Mössbauer atom of mass $m$ is not too large, the Mössbauer fraction at temperature $T$ is given[6] by equation (1). Here $\sigma_s$ is the coefficient of the $s$th normal co-ordinate in the expansion of $\vec{x}m^{\frac{1}{2}}$, the

$$f(T) = \exp(-W) = \exp\{-k^2\cos^2\phi \sum_s \sigma_s^2(\hbar/2m\omega_s). \\ (\{2/[\exp(\hbar\omega_s/\boldsymbol{k}_BT) - 1]\} + 1)\} \quad (1)$$

mass-weighted deviation from the equilibrium position of the Mössbauer atom, $\phi$ is the angle between $\vec{x}$ and $\vec{k}$, the wave factor of the emitted (or absorbed) $\gamma$ quantum. The frequency of the $s$th mode is $\omega_s$, $\boldsymbol{k}_B$ is the Boltzmann constant and $\hbar$ is the Planck constant $\boldsymbol{h}$ divided by $2\pi$. When measuring on a powder one has to average over all the angles $\phi$ and $\overline{\cos^2\phi} = \frac{1}{3}$.

In a molecular crystal the normal modes will in general consist of a quasi-continuous distribution of frequencies, associated with intermolecular vibrations, and a discrete spectrum due to intramolecular vibrations. In that case we obtain (2) where the integration is over the quasi-continuous lattice phonon spectrum $g(\omega)$ and the summation is over the intramolecular vibrations $s'$. In a unimolecular cubic lattice $\sigma(\omega) = (m/MN)^{\frac{1}{2}}$, where $M$ is the molecular mass and $N$ the number of molecules in the lattice. If one describes $g(\omega)$ by the Debye model, $g(\omega) = 9N\omega^2/\omega_D^3$ for $0 < \omega \leqslant \omega_D$ and the first term on the right-hand side of equation (2) becomes (3) where $\theta_D = \hbar\omega_D/\boldsymbol{k}_B$ is the Debye temperature.

$$W(T) = W_L(T) + W_M(T) = \\ \frac{k^2\hbar}{6m}\int_0^\infty \frac{\sigma^2(\omega)}{\omega}\left[\frac{2}{\exp(\hbar\omega/\boldsymbol{k}_BT) - 1} + 1\right]g(\omega)d\omega + \\ \frac{k^2\hbar}{6m}\sum_{s'}\frac{\sigma_{s'}^2}{\omega_{s'}}\left[\frac{2}{\exp(\hbar\omega_{s'}/\boldsymbol{k}_BT) - 1} + 1\right] \quad (2)$$

$$W_L(T) = \frac{k^2\hbar^2}{2M}\cdot\frac{3}{2\boldsymbol{k}_B\theta_D}\left[1 + \frac{4T^2}{\theta_D^2}\int_0^{\theta_D/T}\frac{x\,dx}{e^x - 1}\right] \quad (3)$$

When two different molecules are present in the lattice no simple expression can be given either for $\sigma(\omega)$ or for $g(\omega)$.[7] As a first approximation we will employ equation (3) using for $M$ the molecular weight of the molecule involved in the Mössbauer transition. For an evaluation of the second term, $W_M$, on the right-hand side of equation (2) one needs to know the normal modes and eigenfrequencies of the molecule under investigation. In general, $\hbar\omega_{s'}$ will be of the order of 100 K whereas the measurements have been carried out between 4 and 25 K. In this region the temperature dependence of $W_M$ will be small and consequently can be neglected to a first approximation. Thus we obtain (4) where $W_L(T)$ is given by equation (3) and $W_M = (k^2\hbar/6m)\sum_{s'}(\sigma_{s'}^2/\omega_{s'})$.

$$f(T) = f_L(T)\cdot f_M = \exp[-W_L(T) - W_M] \quad (4)$$

## EXPERIMENTAL

Mössbauer spectra (Table 2) of six compounds were measured as a function of temperature. Two of these are mixed-valence compounds. The spectra were recorded with a constant-acceleration spectrometer and a triangular variation of the velocity. An integrating counting technique[8] was used. All the measurements on one absorber were carried out with the same source. In order to correct for the decay of the source, which has a half-life of 18 h, measurements at >4.2 K were alternated with those at

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[5] F. H. Brain, C. S. Gibson, J. A. J. Jarvis, R. F. Phillips, H. M. Powell, and A. Tyabji, *J. Chem. Soc.*, 1952, 3686.

[6] B. Kaufman and H. L. Lipkin, *Ann. Physique*, 1962, **18**, 294.

[7] Yu. Kagan and V. A. Maslov, *Soviet Phys. JEPT*, 1962, **14**, 922.

[8] M. P. A. Viegers and J. M. Trooster, *Nucl. Instr. Methods*, 1974, **118**, 257.

TABLE 2

Results of measurements on the temperature dependence of the Mössbauer fraction $f$

| Compound | Ref.[a] | Molecular mass $M$/g mol$^{-1}$ | Q.s. (mm s$^{-1}$) | I.s. (mm s$^{-1}$) | $\theta_D$/K | $f_M$ | $f_L$ (4.2 K) | $f_{expt.}$ (4.2 K) |
|---|---|---|---|---|---|---|---|---|
| $[AuBr_2\{S(CH_2Ph)_2\}]$ | 5 | | | | | | | |
| $Au^I$ | | 491 | 5.92 | 0.57 | 53 | 0.36 | 0.11 | 0.040 |
| $Au^{III}$ | | 651 | 1.93 | 0.94 | 53 | 0.40 | 0.19 | 0.078 |
| $[AuBr\{S(CH_2Ph)_2\}]$ | 5 | 491 | 5.99 | 0.96 | 48 | 0.33 | 0.094 | 0.032 |
| $[AuBr_3\{S(CH_2Ph)_2\}]$ | 5 | 651 | 2.46 | 1.47 | 52 | 0.41 | 0.18 | 0.074 |
| $[AuCl_2\{S(CH_2Ph)_2\}]$ | 5, *b* | | | | | | | |
| $Au^I$ | | 447 | 6.35 | 1.05 | 58 | 0.31 | 0.11 | 0.036 |
| $Au^{III}$ | | 518 | 2.16 | 1.38 | 58 | 0.47 | 0.15 | 0.073 |
| $[AuBr_2(S_2CNBu_2)]$ | *c* | 561 | 2.20 | 1.47 | 47 | 0.33 | 0.11 | 0.046 |
| $[\{Au(S_2CNPr_2)\}_2]$ | 12 | 732 | 6.39 | 1.80 | 45 | 0.24 | 0.18 | 0.040 |

[a] For preparation and structure. [b] F. Hessmann, *Ber.*, 1905, **38**, 2813. [c] P. T. Beurskens, J. A. Cras, Th. W. Hummelink, and J. G. M. van der Linden, *Rec. Trav. chim.*, 1970, **89**, 984.

4.2 K. The absorption intensity was calibrated by measurements on a gold foil of known thickness, preceding and following each series of measurements on a compound. Details of the procedure used to determine the effective absorber thickness $T_a$ from the spectra can be found elsewhere.[9] In cases where the individual lines have considerable overlap, the effective absorber thickness could be determined directly from a least-squares fit using a transmission integral.[10] Examples of such fits are given in Figure 2. The two spectra obtained in one measurement were treated independently and the results agreed within the limits of the estimated errors. From the average value of $T_a$ the Mössbauer fraction was determined from $T_a = fn\sigma_0$, where $n$ is the number of $^{197}$Au nuclei cm$^{-2}$ and $\sigma_0$ is the cross section for absorption. We estimate the accuracy in the determination of $n$ to be 5% and this produces by far the largest uncertainty in $f$, when comparing different samples, but has no effect, of course, on the relative temperature dependence.

The values of $f(T)$ thus found were subsequently fitted to equation (4), $\theta_D$ and $f_M$ being the only variables. The integral in equation (3) was evaluated numerically using the Simpson integration technique.[11] For the mixed-valence compounds, the $f(T)$ values of both sites were fitted simultaneously using one value of $\theta_D$. Examples of these fits are given in Figure 3.

Finally we determined $f$ for a number of compounds of $Au^I$ and $Au^{III}$ at 4.2 K.

## RESULTS AND DISCUSSION

The results of the measurements and analysis are given in Table 2. In agreement with the molecular nature of all the compounds investigated, the values of $\theta_D$ are small and of the same order of magnitude. It is also clear that the difference in Mössbauer intensity between compounds of $Au^I$ and $Au^{III}$ is to a large extent due to the difference in molecular weight, although the larger degree of freedom for the Au atom in the linear gold(I) compounds also contributes. Even at 4.2 K the total Mössbauer fraction is appreciably attenuated by the contribution of intramolecular vibrations. The values obtained for $[\{Au(S_2CNPr^n_2)\}_2]$ deviate somewhat from the other compounds. In this compound the molecules occur as dimers,[12] and we therefore used the mass of the dimer in equation (3). The low value of $f_M$ may be due to additional degrees of freedom within the dimeric unit, such as a torsional motion.

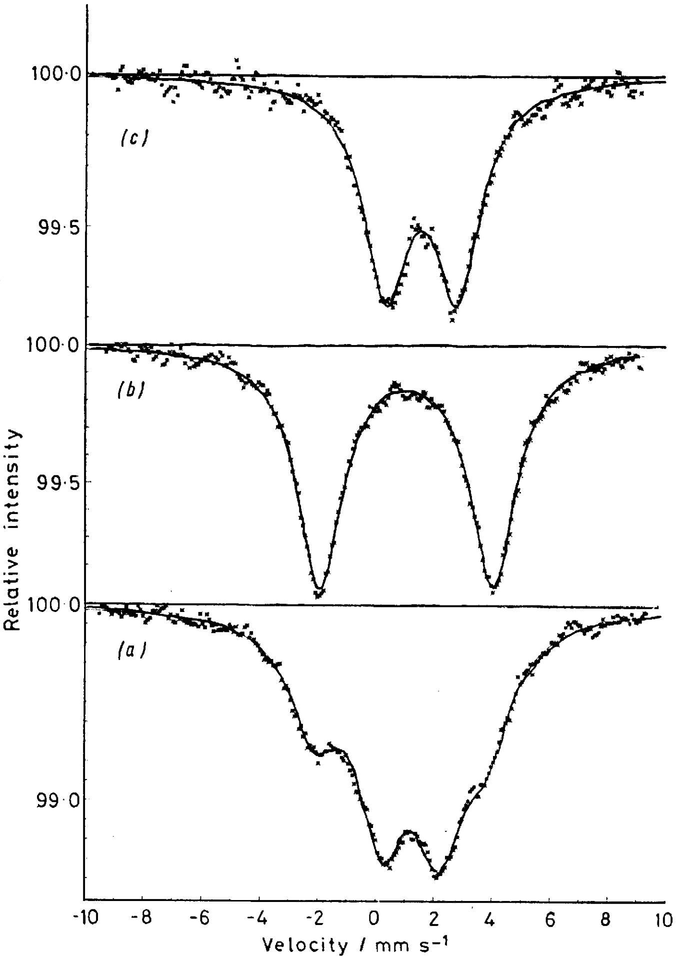

FIGURE 2 Mössbauer spectra of (*a*) the mixed-valence gold compound $[AuBr_2\{S(CH_2Ph)_2\}]$, (*b*) $[AuBr\{S(CH_2Ph)_2\}]$, and (*c*) $[AuBr_3\{S(CH_2Ph)_2\}]$. The full lines are least-squares fits of the transmission integral

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[9] M. P. A. Viegers and J. M. Trooster, *Phys. Rev.*, 1977, **B15**, 72.

[10] G. K. Shenoy, J. M. Friedt, H. Maletta, and S. L. Ruby, ' Mössbauer Effect Methodology,' 1974, vol. 9.

[11] R. W. Hamming, ' Numerical Methods for Scientists and Engineers,' McGraw-Hill, London, 1962.

[12] R. Hesse and P. Jennische, *Acta Chem. Scand.*, 1972, **26**, 3855.

The values for $f_M$ should correspond to reasonable values of $\omega_{s'}$ when the expression for $W_M$ given in equation (2) is used. In order to derive an order of magnitude of $f_M$ for $Au^{II}$, we used the normal modes and frequencies of $[AuBr_4]^-$ given in Figure 4. Of the nine normal modes, five have non-zero values of $\sigma_{s'}$. The expressions for $\sigma_{s'}^2$ are given in (5). Using the fre-

$$\sigma^2(A_{2u}) = \frac{4m_{Br}}{m_{Au} + 4m_{Br}} \text{ and } \sigma^2(E_u) = \frac{2m_{Br}}{m_{Au} + 2m_{Br}} \quad (5)$$

quencies given in Figure 4, we calculate $W_M$ for $[AuBr_4]^-$ to be 0.75, which gives $f_M = 0.47$, in excellent agreement with the values of $f_M$ derived for $Au^{III}$ from the experimental data. For the linear $[AuBr_2]^-$ moiety we calculate $W_M = 1.05$, assuming the bend vibration ($\Pi_u$) and the asymmetrical stretch vibration ($\Sigma_u^+$) to have wavenumbers of 40 and 300 cm$^{-1}$, respectively, as determined for $HgBr_2$.[13] This gives $f_M = 0.35$, again in agreement with the values found experimentally. Support for this interpretation can also be found in the spectrum of $Cs_2Au^IAu^{III}Cl_6$, which crystallizes in an ionic structure, whence no effects on $f$ of different molecular weights can be expected. Accordingly the intensity ratio of the absorption lines of $Au^I$ and $Au^{III}$ is *ca.* 0.75 : 1.[14]

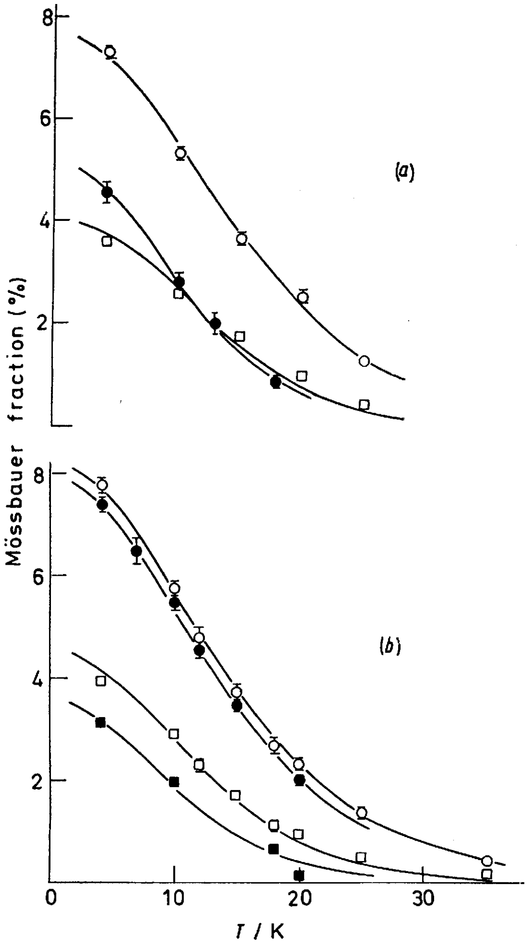

FIGURE 3 Temperature dependence of the Mössbauer fraction. The full lines are least-squares fits (see text). Compounds: (*a*) $[AuCl_2\{S(CH_2Ph)_2\}]$ [(○) $Au^{III}$ site, (□) $Au^I$ site] and $[AuBr_2(S_2CNBu_2)]$ (●); (*b*) $[AuBr_2\{S(CH_2Ph)_2\}]$ [sites as in (*a*)], $[AuBr_3\{S(CH_2Ph)_2\}]$ (●), and $[AuBr\{S(CH_2Ph)_2\}]$ (■)

The formulae used do not take into account directional effects in the cross section for Mössbauer absorption, which can lead to intensity differences between the absorption lines of a quadrupole pair, the so-called Goldanskii–Karyagin effect. However, Prosser *et al.*[15] showed that this effect is small for $^{197}Au$ due to the mixture of $M_1$ and $E_2$ radiation.

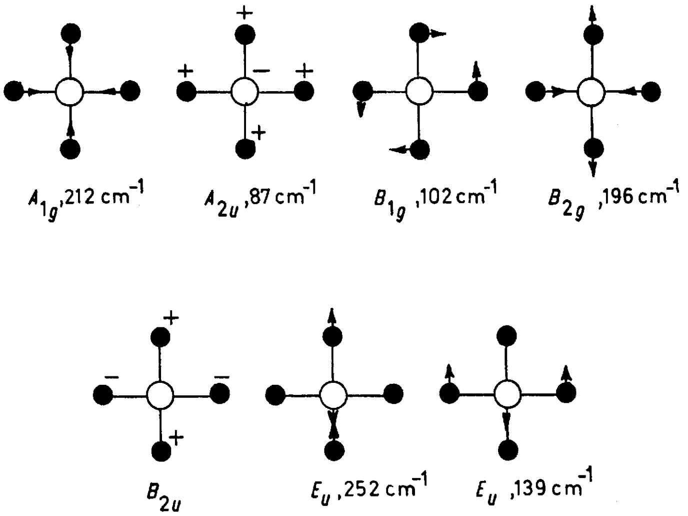

FIGURE 4 Normal modes of $AB_4$ ($D_{4h}$). The wavenumbers given are those [13] of $[AuBr_4]^-$

The conclusion that the molecular mass explains to a large extent the differences in Mössbauer fraction of $^{197}Au$ in molecular complexes is corroborated by the results of measurements on $f$ ($T$ 4.2 K) for a large number of compounds (Tables 3 and 4). Neglecting differences in $f_M$ for compounds with the same oxidation state of gold, the Mössbauer fraction at 4.2 K is proportional to $f_L$. At this temperature equation (3) reduces to (6), and, neglecting differences in $\theta_D$ for

$$W_L = \frac{k^2\hbar^2}{2M} \cdot \frac{3}{2k_B\theta_D} \quad (6)$$

different compounds, it follows from (6) that $-\ln f$ (4.2 K) should be proportional to $M^{-1}$. This relation is reasonably fulfilled for gold(I) compounds (Figure 5). However, extrapolating to infinite mass gives $f_M \simeq 0.11$ which is too low. This indicates that $\theta_D$ depends on $M$ as well. It is interesting to note that for $Au[S_2P(OPr^i)_2]$ the mass of the monomer has to be taken, in spite of

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[13] H. Siebert, 'Anwendungen der Schwingungsspektroskopie in der Anorganische Chemie,' Springer Verlag, Berlin, 1966.

[14] M. O. Faltens and D. A. Shirley, *J. Chem. Phys.*, 1970, **53**, 4249.

[15] H. Prosser, F. E. Wagner, G. Wortmann, and G. M. Kalvius, *Hyperfine Interactions*, 1975, **1**, 25.

the dimeric structure reported by Lawton *et al.*[16] For gold(III) compounds (Figure 6) the assumptions underlying the relation between $-\ln f$ and $M^{-1}$ seem to hold less well.

TABLE 3

Mössbauer fraction $f$ at 4.2 K of some gold(I) compounds

| No. in Figure 5 | Compound | Ref. [a] | Formula weight | $f$ |
|---|---|---|---|---|
| 1 | $[Au_2Cu_4(C_6H_4NMe_2\text{-}2)_4(O_3CSF_3)]$ | *b* | 1 427 | 0.083 |
| 2 | $[Au_2Cu_4(C_6H_4NMe_2\text{-}2)_4I_2]$ | *b* | 1 383 | 0.077 |
| 3 | $[Au_2Cu_2\{C_6H_4(CH_2NMe_2\text{-}2)\}_4]$ | *c* | 1 126 | 0.067 |
| 4 | $[Au_2Li_2(C_6H_4NMe_2\text{-}2)_4]$ | *b* | 889 | 0.053 |
| 5 | $[AuCl(PPh_3)_2]$ | *d* | 757 | 0.058 |
| 6 | $[\{Au(S_2CNPr_2)\}_2]$ | 12 | 732 | 0.040 |
| 7 | $[Au(C_6H_4NMe_2\text{-}2)(PPh_3)]$ | *b* | 597 | 0.042 |
| 8 | $[AuI(PPh_3)]$ | *e* | 586 | 0.040 |
| 9 | $[Au(SCN)(PPh_3)]$ | *e* | 517 | 0.040 |
| 10 | $[AuCl(PPh_3)]$ | *e* | 495 | 0.038 |
| 11 | $[AuBr_2\{S(CH_2Ph)_2\}]$ ($Au^I$ moiety) | 5 | 491 | 0.040 |
| 12 | $[AuBr\{S(CH_2Ph)_2\}]$ | 5 | 491 | 0.030 |
| 13 | $[Au(CN)(PPh_3)]$ | *f* | 485 | 0.032 |
| 14 | $[AuCl_2\{S(CH_2Ph)_2\}]$ ($Au^I$ moiety) | 5 | 447 | 0.036 |
| 15 | $[Au(C_6H_{11})(CN)(C_6H_4NMe_2\text{-}2)]$ | *b* | 426 | 0.039 |
| 16 | $[Au\{S_2P(OPr^i)_2\}]$ | 16 | 410 | 0.023 |

[a] For preparation and structure. [b] G. van Koten, J. T. B. H. Jastszzebski, and J. G. Noltes, *Inorg. Chem.*, 1977, **16**, 1782. [c] G. van Koten and J. G. Noltes, *J. Organometallic Chem.*, 1974, **82**, C53. [d] N. C. Baenziger, K. M. Dittemore, and J. R. Doyle, *Inorg. Chem.*, 1974, **13**, 805. [e] G. E. Coates and C. J. Parkin, *J. Chem. Soc.*, 1962, 3220. [f] D. I. Nichols and A. S. Charleston, *J. Chem. Soc. (A)*, 1969, 258.

TABLE 4

Mössbauer fraction $f$ at 4.2 K of some gold(III) compounds

| No. in Figure 6 | Compound | Ref. [a] | Formula weight | $f$ |
|---|---|---|---|---|
| 1 | $[AuBr_2\{S(CH_2Ph)_2\}]$ ($Au^{III}$ moiety) | 5 | 651 | 0.078 |
| 2 | $[AuBr_3\{S(CH_2Ph)_2\}]$ | 5 | 651 | 0.074 |
| 3 | $[AuBrI(S_2CNBu_2)]$ | *b* | 608 | 0.051 |
| 4 | $[AuBr_2(S_2CNBu_2)]$ | *b* | 561 | 0.046 |
| 5 | $[AuCl_2\{S_2CN(C_7H_{15})_2\}]$ | *b* | 556 | 0.065 |
| 6 | $[AuCl_2\{S(CH_2Ph)_2\}]$ ($Au^{III}$ moiety) | 5 | 518 | 0.073 |
| 7 | $[NBu_4][Au\{S_2C_2(CN)_2\}]$ | *c* | 477 | 0.044 |
| 8 | $[AuMe_2(S_2CNBu_2)]$ | *b* | 431 | 0,032 |
| 9 | $[AuMe_2(S_2CNPr_2)]$ | *b* | 403 | 0.029 |
| 10 | $[AuMe_2(S_2CNMe_2)]$ | *b* | 347 | 0.040 |

[a] For preparation and structure. [b] H. J. A. Blaauw, R. J. F. Nivard, and G. J. M. van der Kerk, *J. Organometallic Chem.*, 1964, **2**, 236. [c] A. Davison, N. Edelstein, R. H. Holm, and A. K. Maki, *Inorg. Chem.*, 1963, **2**, 1227.

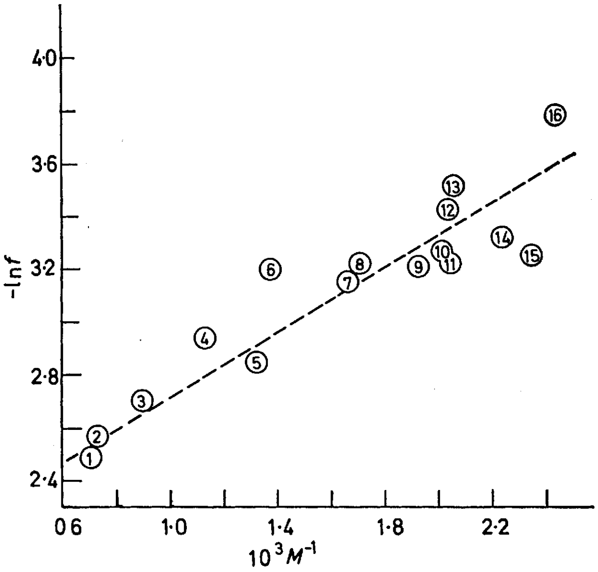

FIGURE 5 Relation between $1/M$ ($M$ = molecular weight) and $-\ln f$ ($f$ = Mössbauer fraction). The numbers refer to the gold(I) compounds listed in Table 3

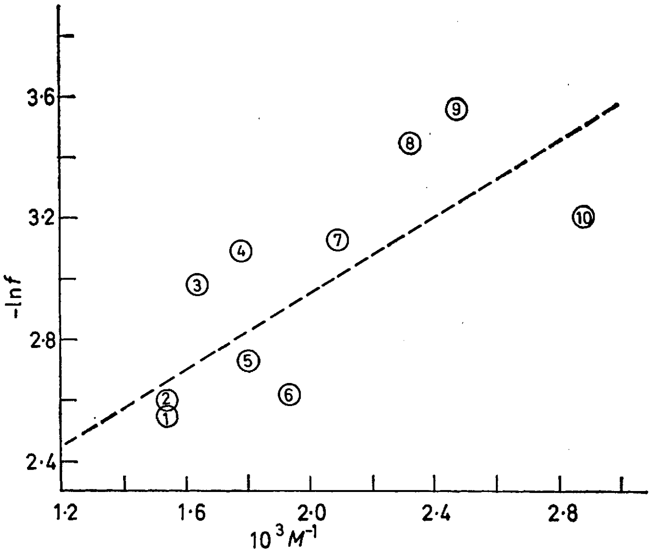

FIGURE 6 Relation between $1/M$ ($M$ = molecular weight) and $-\ln f$ ($f$ = Mössbauer fraction). The numbers refer to the gold(III) compounds listed in Table 4

Finally we point out the implications of our results for the interpretation of the Mössbauer fraction of the more commonly studied $^{57}Fe$ and $^{119}Sn$ in molecular crystals. From equation (3) it can be seen that for $f_L$ the most important difference between $^{197}Au$ and $^{57}Fe$ or $^{119}Sn$ is the value of $k^2$. Thus, assuming that the Debye temperature and molecular mass are comparable, we obtain equation (7) and similarly for $^{119}Sn$. Values of $f_L$

$$\ln f_L(^{57}\mathrm{Fe}) = [E_\gamma^2(^{57}\mathrm{Fe})/E_\gamma^2(^{197}\mathrm{Au})] \ln f_L(^{197}\mathrm{Au}) \quad (7)$$

calculated from equation (3) for a molecular mass $M$ = 500 and a Debye temperature $\theta_D$ = 60 K are given in Table 5 for these three nuclei. For $f_M$ such an extrapolation of our results is more difficult because both $\omega_{s'}$ and $\sigma_{s'}$ depend on the mass of the Mössbauer nucleus. As a first approximation we may assume that the main difference is caused by the nuclear parameter $E_R = k^2\hbar^2/2m$, the recoil energy. Then we obtain equation (8).

$$\ln f_M(^{57}\mathrm{Fe}) = [E_R(^{57}\mathrm{Fe})/E_R(^{197}\mathrm{Au})] \ln f_M(^{197}\mathrm{Au}) \quad (8)$$

Values of $f_M$ calculated for a single isotropic mode with $\hbar\omega/k$ = 150 K and $\sigma_{s'}$ = 1 are also given in Table 5.

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[16] S. L. Lawton, W. J. Rohrbaugh, and G. T. Kokotailo, *Inorg. Chem.*, 1972, **11**, 2227.

From this Table it is clear that the assumption that the intermolecular lattice vibrations determine mainly the Mössbauer fraction in molecular crystals is reasonable for $^{119}$Sn, but much less so for either $^{197}$Au or $^{57}$Fe. Furthermore, the observation of a Goldanskii–Karyagin effect in molecular crystals should not be correlated automatically with anisotropy in the intramolecular vibrations, but can equally well be due to anisotropy in the vibration amplitude of the molecule as a whole.

TABLE 5

Values of $f_L$ and $f_M$ for the three nuclei $^{197}$Au, $^{119}$Sn, and $^{57}$Fe: $f_L$ was calculated from equation (3) with $M = 500$ and $\theta_D = 60$ K; $f_M$ was calculated from equation (2) using one oscillator with $\sigma_{s'} = 1$ and $\omega_{s'} = 150$ K

| | $f_L$(%) | | | $f_M$(%) | | |
|---|---|---|---|---|---|---|
| $T$/K | $^{197}$Au | $^{119}$Sn | $^{57}$Fe | $^{197}$Au | $^{119}$Sn | $^{57}$Fe |
| 4.2 | 0.145 | 0.83 | 0.94 | 0.28 | 0.82 | 0.86 |
| 77 | $7 \times 10^{-4}$ | 0.40 | 0.72 | 0.18 | 0.77 | 0.82 |
| 300 | | 0.03 | 0.28 | 0.006 | 0.44 | 0.54 |

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