Mean Amplitudes of Vibration for PMo$_{12}$O$_{40}^{3-}$ and Its Fragments

S. J. Cyvin$^a$,*, L. Lyhamn$^b$, and B. N. Cyvin$^a$

$^a$ Division of Physical Chemistry, The University of Trondheim, N-7034 Trondheim-NTH, Norway

$^b$ Department of Inorganic Chemistry, The University of Umeå, S-901 87 Umeå, Sweden

(Received 3 April 1978. Accepted 26 April 1978)

Mean amplitudes of vibration ($l$) are calculated for all 80 distance types in PMo$_{12}$O$_{40}^{3-}$. The values are discussed and some of them compared with the corresponding values calculated for five different fragments of the structure. Reasonable $l$ values (< 0.12 Å at 298 K) are found even for extremely long distances, e.g. 0.078 Å at 298 K for the longest oxygen—oxygen distance (10.4 Å). The $l$ values for bonded distances as well as a number of nonbonded distances have comparable magnitudes in the fragments and the whole structure; in other cases the fragment values are substantially higher.

(Keywords: Force field, calculation of mean amplitudes of vibration; PMo$_{12}$O$_{40}^{3-}$; Vibration, mean amplitudes of)

Mittlere Schwingungsamplituden für PMo$_{12}$O$_{40}^{3-}$ und Fragmente

Mittlere Schwingungsamplituden ($l$) für alle 80 Typen von Abständen in PMo$_{12}$O$_{40}^{3-}$ wurden berechnet. Die Werte werden diskutiert und einige werden mit denen von fünf verschiedenen Fragmenten der untersuchten Struktur verglichen. Es wurden auch für extrem große Distanzen plausible $l$-Werte (< 0.12 Å bei 298 K) gefunden (z. B. 0.078 Å bei 298 K für die größte O—O-Distanz 10.4 Å). Die $l$-Werte für Bindungslängen und auch für einige Abstände von nicht aneinander gebundenen Atomen weisen in den Fragmenten und in der Gesamtstruktur vergleichbare Größe auf; in anderen Fällen sind die Fragment-Werte allerdings bedeutend höher.

Introduction

A vibrational analysis of PMo$_{12}$O$_{40}^{3-}$ ($T_d$ symmetry) has been described previously$^{1,2}$. In the present work the forcefield described in Ref.$^1$ was used to calculate the mean amplitudes of vibration ($l$)$^3$ for the
PMo_{12}O_{40}^{3-} ion. The quantities are defined as

$$l = \langle (\Delta r)^2 \rangle$$

i.e. the root-mean-square deviations of interatomic distance as a result of molecular vibrations. The mean value is taken both in the quantum-mechanical and the statistical-mechanical sense. Hence the $l$ values are temperature-dependent quantities. For further details the standard reference may be consulted.

To our knowledge this is the largest structure (53 atoms) for which the computations of mean amplitudes have been successfully completed from a complete analysis according to the theory of small harmonic vibrations. Since the considered structure is an ion the calculated mean amplitudes are not the subject of immediate application in gas electron diffraction studies. Nevertheless they are supposed to be of special interest for several other reasons: (1) The results give us the opportunity to study, in general terms, the behaviour of mean amplitudes for very long nonbonded interatomic distances, namely up to 10.4 Å. (2) Calculated mean amplitudes for different fragments of the structure may be compared with the results for the corresponding distances in the whole ion. Thus it is possible to judge the validity of transferring mean amplitudes from fragments to the whole compound in cage structures like the one of the present investigation. (3) Finally the calculated mean amplitudes for ions as well as molecules are of general interest because they are physical quantities associated with the different bonded and nonbonded atom pairs. Those of the bonded pairs reflect the bond strength generally in a more meaningful way than the force constants.

In the present work the mean amplitudes ($l$ values) were calculated at the temperatures of absolute zero and 298 K. Simultaneously the perpendicular amplitude correction coefficients ($K$ values) were obtained. For sake of brevity only the $l$ values at 298 K are reported and discussed here.

**Molecular Model**

A tetrahedral model ($T_d$; see Fig. 1) was assumed for the PMo_{12}O_{40}^{3-} ion (a). It is an idealization of a structure deduced from single crystal data. The central atom, P, is surrounded tetrahedrally by four oxygen atoms, O (P); see Fig. 2 (b). Each of the O (P) atoms forms the apex of a trigonal MoO$_3$ group as shown in Fig. 2 (d). This fragment contains a puckered Mo$_3$O$_7$ ring. The four Mo$_3$O$_7$ groups are linked together by Mo—O—Mo bonds, which may be referred to as interligand bridges if the Mo$_3$O$_7$ groups are interpreted as ligands. It should be mentioned that the concept of ligands in this case was introduced from a mathematical viewpoint rather than a chemical one. The oxygen atoms of the in-