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A Mössbauer study of xenon compounds

Hendrik de Waard
Laboratorium voor Algemene Natuurkunde, University of Groningen, The Netherlands

Shmuel Bukshpan
Soreq Nuclear Research Center, Yavne 70600, Israel

Gary J. Schrobilgen
Department of Chemistry, University of Guelph, Guelph, Ontario, N1G 2W1, Canada

John H. Holloway
Department of Chemistry, University of Leicester, Leicester LE1 7RH, England

Dominique Martin
Département de Génie Isotopique, Centre d’Études Nucléaires de Saclay, B.P. No. 2, 91190 Gif-sur-Yvette, France

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A large number of xenon compounds have been synthesized and studied by nuclear gamma resonance of the 39.6 keV transition in $^{129}$Xe. The quadrupole interaction strengths (Q.S.) of all divalent xenon compounds with linear F-Xe-F groups lie close together, but a small increase of the Q.S. with the acceptor strength of adduct groups is observed. For compounds with F-Xe-O- and -O-Xe-O- groups a reduction of the Q.S. of up to 10% is found. The tetravalent compounds exhibit a Q.S. with absolute magnitude very close to that of the divalent compounds, consistent with a square planar configuration and nearly equal contributions to the Q.S. for each Xe-F bond. Hexavalent xenon in XeF$_6$ also exhibits an appreciable Q.S., indicative of distortion of the octahedral fluorine configuration around the xenon atom in the polymeric solid. An increase of the Q.S. relative to XeF$_6$ is observed in the adducts and in hexavalent compounds with mixed oxygen/fluorine bonding. This is interpreted as due to increased distortion around the central xenon atom.

INTRODUCTION

The chemistry of xenon compounds originated in 1962 and since then an impressive number of such compounds have been synthesized and their structures studied by a variety of techniques.\(^1\)

The Mössbauer effect of the 39.6 keV transition in $^{129}$Xe was already used in the early stages of xenon chemistry to study the hyperfine interaction of xenon in some of its compounds and to supply values for the quadrupole moment of the 39.6 keV state, the electric field gradients, and contact electron densities of xenon in these compounds.\(^2\) Several of the compounds that were first produced in the radioactive decay of $^{129}$I to $^{129}$Xe have been subsequently synthesized in the laboratory. For some, such as XeBr$_2$, the only established route to synthesis is still by $\beta$ decay of $^{129}$I.

In the present work we report the results of a study of a series of 21 compounds, which have been synthesized in the laboratory. The objective of this study is to add to our understanding of the bonding in xenon compounds by measuring the quadrupole coupling and the isomer shift. The compounds in this work can be divided into four groups according to the formal oxidation state of the central xenon atom.

In the first group, xenon is in the divalent state. This group consists of XeF$_2$ and its adducts. The adducts belong to two broad categories, those in which the ionic valence-bond structure (I) dominates and those in which the covalent valence-bond structure (II) dominates:

\[
\begin{align*}
\text{I} & : \quad \text{F-Xe}^+\text{F}^- \quad \text{F-Xe}^-\text{F}^+ \\
\text{II} & : \quad \text{F-Xe}^+\text{F}^- \\
\end{align*}
\]

where A represents the neutral fluoride ion acceptor species. A linear F-Xe---F group in which the bond length between xenon and the terminal fluorine is shorter than that between xenon and the bridging fluorine is present in all of the adducts and is generally referred to as a "fluorine bridge." The "ionic," weakly fluorine-bridged adducts are represented in this study by XeF$_2$·TaF$_5$, XeF$_2$·BiF$_3$, and XeF$_2$·Sb$_2$F$_7$, while the "covalent" more strongly fluorine-bridged adducts are represented by XeF$_2$·MoOF$_4$ and XeF$_2$·WO$_3$F$_2$. The Mössbauer spectrum of the XeF$_2$ cation in the AsF$_5$ and BiF$_6$ salts has also been recorded. The x-ray crystal structure of XeF$_2$·AsF$_5$ has shown that the V-shaped, strongly fluorine-bridged XeF$_2$ cation is not fluorine-bridged to the anion.

Finally, a series of Xe (II) compounds in which xenon is directly bonded to oxygen has been studied. Of the compounds studied, (FXe)$_3$SO$_3$F·AsF$_5$ and Xe(OTeF$_5$)$_2$ had been previously shown to contain F-Xe-O- and -O-Xe-O- groups, respectively. The compound Xe(OTeF$_5$)$_2$·AsF$_5$ is presumed to contain a F-Xe-O-F group.

The tetravalent xenon compounds studied, XeF$_2$·Sb$_2$F$_7$ and XeF$_2$·BiF$_6$, have essentially a square planar...
F\textsubscript{2}Xe---F\textsubscript{2}--- configuration similar to XeF\textsubscript{4}, but with a close contact between the cation and fluorine of the anion. Other long fluorine bridging interactions have also been observed in these structures.

The hexavalent compound XeF\textsubscript{6} and its adducts XeF\textsubscript{6}Sb\textsubscript{2}F\textsubscript{11} and XeF\textsubscript{6}F\textsubscript{2}BIF\textsubscript{6} presumably have distorted octahedral XeF\textsubscript{6} structures. The remaining hexavalent oxygen-containing xenon compounds possess C\textsubscript{6}v and C\textsubscript{1} molecular point group symmetries in the case of XeOF\textsubscript{4} and XeO\textsubscript{2}F\textsubscript{2} (in XeO\textsubscript{2}F\textsubscript{2}SbF\textsubscript{6}), respectively.

Finally, in the only available octavalent xenon compound, Na\textsubscript{2}XeO\textsubscript{4}, the xenon has been shown to possess a regular octahedral oxygen environment.

**EXPERIMENTAL**

For most of the measurements a source of Na\textsubscript{3}H\textsubscript{129}I\textsubscript{5}, containing 80 mg of \textsuperscript{129}I (T\textsubscript{1/2} = 1.7 x 10\textsuperscript{7} yr) and having a decay strength of 12 \(\mu\)Cl, was used. Due to the large conversion of the 39.6 keV gamma ray emitted after beta decay of \textsuperscript{129}I, the gamma strength is only 0.5 \(\mu\)Cl, leading to a very low counting rate. However, the source recoilless fraction is quite high (f = 0.34 at liquid helium temperature\textsuperscript{5}) and relatively thick absorbers can be used, so that good spectra were usually obtained in 1--2 day runs. Cyclotron produced \textsuperscript{129}Cs (T\textsubscript{1/2} = 38 h) in CsCl was used a few times as an alternative source. Though of much higher intensity, the cost and labor involved in the preparation of these sources as well as their short half life made us prefer the \textsuperscript{129}I sources.

The syntheses of the absorber materials have been described elsewhere. Relevant references are given in Table I. All of the compounds are stable at ambient temperature in a dry atmosphere. Absorbers were prepared from these compounds using a glove box in which a helium atmosphere with less than 2 ppm of oxygen and 2 ppm of water is maintained.

Quantities of 40--400 mg of absorber material were thoroughly mixed with dried, perfluorinated Teflon powder in 20 mm diam Teflon "pill boxes" sealed with a tightly fitting recessed Teflon lid (Fig. 1). These boxes were clamped between stainless steel top and bottom pieces with 17 mm holes to allow the gamma rays to pass through the absorber material. When loaded, the absorber containers were submerged in liquid nitrogen immediately after removal from the glove box. During transfer to the Mössbauer spectrometer cryostat, the absorber was kept at liquid nitrogen temperature. None of the absorbers thus prepared showed any sign of decomposition.

Owing to their high volatility and sensitivity to moisture, XeOF\textsubscript{4} and XeF\textsubscript{6} were sealed in flat quartz ampoules immediately after transfer on a vacuum line and stored under liquid nitrogen until used.

The 39.6 keV radiation was detected by an intrinsic Ge detector of diameter 22 mm and thickness 5 mm. All spectra were recorded at liquid helium temperature with a standard Mössbauer spectrometer using sinusoidal or triangular velocity waveforms.

**MEASUREMENTS**

The Mössbauer spectra of all compounds except Na\textsubscript{2}XeO\textsubscript{4}, for which a single line is observed, can be decomposed into two Lorentzian lines of about equal depth. Some representative spectra for xenon compounds with different formal Xe oxidation states are given in Fig. 2. The separation, \(\Delta E\), of these lines yields the absolute value of the quadruple interaction strength, \(\mid e^2qQ\mid\), and the center of gravity of the spectrum gives the isomer shift relative to the source, usually Na\textsubscript{3}H\textsubscript{129}I\textsubscript{5}. All measured shifts were converted to the shifts with respect to an absorber of neutral xenon in \(\beta\)–hydroquinone. The hyperfine interaction parameters were derived from two line fits to the experimental spectra, restricting the two lines to equal intensity and width but otherwise leaving all parameters free. These are given in Table I.

The error limits in Table I take into account statistical as well as calibration errors. In most cases the quadrupole splittings were determined with an accuracy better than 1%. On the other hand, the errors in the isomer shifts are comparable in magnitude with the shifts themselves. These are only a small fraction of the natural line width of the 39.6 keV line, typically a few percent. Such small shifts often have no clear physical meaning because they may be affected by small chemical contaminations or by deviations of the line shape from the Lorentzian form used in the computer fits. This seriously limits the amount of information that can be obtained from the isomer shifts. Very careful comparative measurements would be needed to lower limits of error below 1% of the natural width.

The component line width, which was also a free parameter in the fit, lies between 8.8 and 10 mm/s, compared with a natural width 2\(\pi\tau\) = 6.8(3) mm/s. The line broadening can only be partly ascribed to absorber thickness; for a very thin absorber a width of 8.8(2) mm/s remains. Because the line widths obtained for many different absorbers of comparable thickness lie consistently in the range 9--10 mm/s, we believe that most of the line broadening is caused by a residual quadrupole interaction in the source.

**DISCUSSION**

The lack of accuracy of the isomer shifts makes it impossible to derive very detailed conclusions from comparisons of these shifts. Nevertheless, some systematic trends emerge if the averages are considered.
TABLE I. Quadrupole splittings ($\Delta \delta_{Q}$) and isomer shifts ($\delta$) derived from $^{129}$Xe Mössbauer spectra for compounds of xenon in the 0, +2, +4, +6, and +8 oxidation states.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta \delta_{Q}$ (mm/s)</th>
<th>$\delta$ (mm/s)</th>
<th>Xe-F$^b$ bridging (Å)</th>
<th>Xe-F$^b$ terminal (Å)</th>
<th>Xe-O$^b$ (Å)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xe(II)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XeF$_2$</td>
<td>39.7(4)</td>
<td>0.2(2)</td>
<td>2×2,00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XeF$_2$-MoOF$_4$</td>
<td>40.3(6)</td>
<td>0.4(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XeF$_2$-2WOFO$_4$</td>
<td>41.0(3)</td>
<td>0.3(1)</td>
<td>(2.04)$^d$</td>
<td>(1.89) $^d$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>XeF$_2$TaF$_7$</td>
<td>40.8(3)</td>
<td>-0.1(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XeF$_2$BiF$_7$</td>
<td>41.4(1)</td>
<td>0.20(5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XeF$_2$Sb$<em>2$F$</em>{11}$</td>
<td>41.5(2)</td>
<td>0.2(1)</td>
<td>2.35</td>
<td>1.84</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>Xe$_2$F$_4$AsF$_5$</td>
<td>41.3(3)</td>
<td>0.5(1)</td>
<td>2.14</td>
<td>2×1.90</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Xe$_2$F$_4$BiF$_7$</td>
<td>41.4(1)</td>
<td>0.20(5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xe(IV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XeF$_4$</td>
<td>41.04(7)$^2$</td>
<td>0.40(4)$^2$</td>
<td>4×1.953</td>
<td></td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>XeF$_5$Sb$<em>2$F$</em>{11}$</td>
<td>39.6(1)</td>
<td>0.20(6)</td>
<td></td>
<td></td>
<td></td>
<td>14</td>
</tr>
<tr>
<td>XeF$_5$BiF$_7$</td>
<td>41.3(1)</td>
<td>0.30(5)</td>
<td>2.25</td>
<td>1.81; 2×1.93</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>Xe(V)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XeF$_6$</td>
<td>7.7(2)</td>
<td>0.3(1)</td>
<td>e</td>
<td>e</td>
<td></td>
<td>16</td>
</tr>
<tr>
<td>XeF$_7$Sb$<em>2$F$</em>{11}$</td>
<td>12.0(2)</td>
<td>0.38(6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xe$_3$F$_6$BiF$_7$</td>
<td>9.1(2)</td>
<td>0.6(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F$_2$XeSO$_3$F</td>
<td>10.4(2)</td>
<td>0.4(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XeOF$_4$</td>
<td>13.6(2)</td>
<td>0.1(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XeF$_{10}$</td>
<td>18.1(5)</td>
<td>0.5(3)</td>
<td>1.904</td>
<td>4×1.904</td>
<td>1.696</td>
<td>17</td>
</tr>
<tr>
<td>Xe(VIII)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$_4$XeO$_6$</td>
<td>0</td>
<td>-0.08(3)$^{ji}$</td>
<td></td>
<td>0</td>
<td>-0.15(3)$^{ji}$</td>
<td>6×1.85$^f$</td>
</tr>
</tbody>
</table>

$^a$Isomer shifts are relative to central xenon in the clathrate $\beta$-hydroquinone.

$^b$All xenon-ligand bond lengths are derived from x-ray crystallography except those for XeF$_4$, which are derived from neutron-diffraction studies.

$^c$References to crystal structure data.

$^d$Data actually obtained for XeF$_2$-WOFO$_4$.

$^e$See Fig. 5.

$^f$Average value of the Xe-O bond distances in Na$_4$XeO$_4$·6H$_2$O and Na$_4$XeO$_4$·8H$_2$O.

The weighted averages of the shifts for each of the four groups of xenon compounds investigated with xenon in four different valence states as well as the range of shifts within each of these groups are given in Fig. 3. The average values extend the trend observed earlier by Perlow$^4$ for the +2 and +4 oxidation states. In the sequence Xe(0), (II), (IV), and (VI) the shift becomes progressively more positive$^3$ with increasing oxidation state due to transfer of 5p-electron density from the central xenon atom into ligand groups of high electronegativity. This causes a reduction of the 5s screening and hence, an increase in the 5s contact density at the xenon nucleus. For Na$_4$XeO$_6$ a negative isomer shift is observed. This is in keeping with the negative shifts observed$^4$ for octahedrally coordinated iodine compounds in the 7+ oxidation state (e.g., Na$_3$H$_2$I$_6$) and, as in those compounds, must be due to hybridization of the Xe-O bonds, leading to removal of some 5s charge from the xenon, i.e., the valence bond form Xe$^+$-O$^-$ is a significant contributing form.
The spread of the shifts within each group is quite large; it widely overlaps other groups. Part of the spread is due to statistical and, probably, to residual systematic errors. It must be pointed out that for Xe (II), for instance, the total spread amounts to less than 8% of the measured linewidth. No evidence has been found for a systematic dependence of the isomer shift on chemical parameters within any of the groups. It is clear, therefore, that the valence state of xenon in any particular compound cannot be determined from its isomer shift alone.

Xenon (II) compounds

In the terminology of the VSEPR (valence shell electron pair repulsion) rules of Gillespie and Nyholm, the divalent compounds are classified as AX₂E₃, with A the central (noble gas) atom, X a ligand, and E a lone pair of electrons. The bond pairs are repelled by the lone pairs to form a 180° F-Xe-L (L = F or O) angle and the lone pairs arrange themselves symmetrically around the F-Xe-L axis (Fig. 4). The Xe-F bonds cause a p-electron imbalance in the 5p shell which produces an electric field gradient at the xenon nucleus. The p-electron imbalance is often measured by $U_e$, the ratio of the quadrupole splitting $\Delta E_Q$ for a specific compound and $\Delta E_Q^{\infty}$ for an ion with one hole in the 5p shell. Using data from optical and atomic beam measurements, Perlow derived a value $\Delta E_Q^{\infty} = 27.3$ mm/s for the 39.6 keV $3/2^+$ state of $^{129}$Xe with one hole in the 5p shell. Thus, $U_e = 1.44 - 1.50$ is found for XeF₂ and its adducts.

In a linear molecule such as XeF₂, the bonding may be

![Diagram](image-url)
assumed to be due only to 5p electrons and, in a simple atomic model, the electric field gradient at the Xe nucleus is then taken as proportional to the number of electrons removed from the 5p shell. This results in $h'_n = U'_n$, meaning that about 1.5 electrons have been removed from the 5p shell. Such a model has been shown to work for linear compounds of iodine, where the number of holes in the 5p shell can be determined independently from the isomer shift. The validity of this model cannot be checked for the xenon compounds in the same way, since the isomer shift calibration of Perlow\(^5\) makes use of the supposed equality $h'_n = U'_n$. There is, however, an ESCA result of Karlsson et al.\(^6\) which places a charge +1 on xenon in XeF\(_2\) and therefore casts some doubt on the validity of the simple atomic model.

NMR\(^7\) and Raman\(^8\) spectroscopy studies indicate that the ionicity of XeF\(_2\) adducts increases with the fluoride acceptor strength of the adducted group. X-ray analyses further show that the length of the bridging Xe-F bond increases with acceptor strength, as expected for increasing ionicity. At the same time the terminal Xe-F bond length decreases.

We have observed a slight increase of the quadrupole interaction strength with acceptor strength, as shown in Table I, where the acceptor strength of the adducted group increases from top to bottom. Therefore, there also exists a correlation between bond length difference and quadrupole interaction strength, similar to that previously found for adducts of KrF\(_2\).\(^9\) As in that case, the observed correlation cannot be explained quantitatively. In particular, no unique relation exists between the quadrupole interaction strength and the terminal and bridging bond lengths. We can only draw the qualitative conclusion that the effect of fluoride-bridge formation on the electric field gradient at the xenon nucleus is almost completely compensated for by a corresponding shortening of the terminal Xe-F bond.

It would be interesting to perform molecular orbital calculations for an F-Xe-F chain with variable F-Xe distances and to compare electric field gradient values derived from such calculations with experimental results.

From the point of view of Mössbauer spectroscopy, the dinuclear Xe\(_2\)F\(_4\)\(^+\) cation is indistinguishable from the mononuclear F-Xe-\(-\)F- cations. In the case of Xe\(_2\)F\(_4\)AsF\(_6\), x-ray analysis shows an ionic crystal structure with clearly separate Xe\(_2\)F\(_4\) and AsF\(_6\) units.\(^10\) The two terminal F-Xe-F groups of the Xe\(_2\)F\(_4\) cation (structure III) make a 150° angle at the central bridging fluoride atom. The terminal Xe-F bond is shorter than the bridging bond and the Q.S. is again slightly enhanced [\(\Delta E_O = 41.4(3)\) mm/s] over that of XeF\(_2\). The compound Xe\(_2\)F\(_4\)BiF\(_6\) with unknown crystal structure, also has an enhanced Q.S. [\(\Delta E_O = 41.4(1)\) mm/s]. From this we may conclude that it has a bond length difference comparable with that of Xe\(_2\)F\(_4\)AsF\(_6\):

Some xenon (II) compounds in which xenon is directly bonded to oxygen were studied. For (F\(\text{Xe}\))\(_2\)S\(_4\)F\(_2\)\(^{+\text{AsF}}\), the chemical structure has been investigated by NMR and Raman spectroscopy\(^11\) as well as by x-ray analysis\(^12\):

\[
F\text{-Xe-O}---\text{O-Xe-F}
\]

IV

These investigations all show a fluorosulfate bridged (F\(\text{Xe}\))\(_2\)S\(_4\)F\(^{+\text{AsF}}\) cation (structure IV) which does not interact with the AsF\(_6\)\(^-\) anion. X-ray analysis yields a terminal F-Xe bond length of 1.86 Å and an Xe-O bridging bond length of 2.21 Å. The quadrupole splitting, \(\Delta E_O = 40.5(4)\) mm/s, is a little smaller than for the species with F-Xe---F chains and similar bond length differences. This indicates a somewhat smaller charge transfer in the Xe-O bond than in the Xe-F bond.

The reduction of charge transfer is more strongly evident in the compounds XeOF\(_2\)F\(_2\)AsF\(_6\) [\(\Delta E_O = 37.4(1)\) mm/s] and Xe(OTeF\(_5\))\(_2\) [\(\Delta E_O = 36.3(3)\) mm/s] and supports structures with F-Xe-\(-\)F and -O-Xe-O- chains, respectively.

**Xenon (IV) compounds**

In the Gillespie-Nyholm notation, these compounds are characterized as AX\(_2\)F\(_2\) (see Fig. 4). The repulsion of the 4 bond pairs by the 2 lone pairs should yield a square planar configuration of the fluorine atoms around the xenon. X-ray analysis bears out this hypothesis for XeF\(_2\) and essentially also for the adducts XeF\(_2\)BiF\(_6\)\(^13\) and XeF\(_2\)SbF\(_6\)\(^14\). Again, however, for the adducts the shortest Xe---F bridging bond is longer and the three Xe-F terminal bonds are shorter than the Xe-F bond in XeF\(_4\). Furthermore the ligand F-Xe-F angles deviate from 90°.

As shown in Table I the quadrupole splitting is affected only very slightly by these distortions: for all three tetravalent compounds investigated it lies in the narrow range \(\Delta E_O = 39.6-41.3\) mm/s.

If, in a square planar configuration, the charge transfer per \(\rho_n\) and \(\rho_p\) bond is equal to the charge transfer per \(\rho_n\) bond in a linear divalent Xe compound, the quadrupole splitting in the square planar configuration should be equal in magnitude and opposite in sign to that for the linear configuration (cf., for example, the discussion of iodine compounds in Ref. 4). The near equality of \(\Delta E_O\) for divalent and tetravalent fluorine bonding xenon compounds supports this assumption.

**Xenon (VI) compounds**

The VSEPR rules, which characterize monomeric XeF\(_4\) as belonging to the AX\(_2\)E class of compounds, give a less definite prescription for the geometry in this case than for the divalent and tetravalent compounds. It should be expected, however, that the regular octahedral arrangement of 8 fluorines around the central xenon atom is distorted by the repulsive effect of an ad-
dential lone pair in the xenon valence shell. Extensive electron diffraction investigations in the gas phase\(^\text{15}\) and x-ray analysis in the solid phase of XeF\(_6\)\(^\text{16}\) show that such a distortion exists and that it is different in both cases.

The crystalline structure is, however, more complex. A cubic unit cell contains 24 tetramers and 9 hexamers of XeF\(_6\) in which XeF\(_2\) groups are bound through fluorine bridges. The geometry of the molecules is slightly different in the tetrameric (I) and the hexameric (II) units. In Fig. 5 a schematic representation is given of the XeF\(_2\) groups. The bond lengths and angles relevant to our discussion are also indicated. In each unit cell there are 96 molecules of type I and 48 of type II.

For an undistorted octahedron with equal Xe–F bond lengths zero quadrupole coupling is expected since, in that case, equal charge is transferred from the \(p_x, p_y\), and \(p_z\) orbitals to fluorine ligands and spherical charge symmetry is preserved at the xenon nucleus. The effect of distortion on the electric field gradient may be estimated by assuming that each ligand making a bond angle \(\alpha\) with the \(z\) axis contributes an amount,

\[
q = q_0 \left( \frac{1}{3} \cos^2 \alpha - \frac{1}{2} \right),
\]

to the \(z\) component of the electric field gradient.

We see in Fig. 5 that the 4 ligands in the basal plane make equal bond angles \(\alpha\) with the \(z\) axis. Along this axis we find the terminal Xe–F bond and the bridging bond to other XeF\(_2\) units in opposite directions, as in the XeF\(_4\) adducts discussed previously. For those compounds, it was found that the total quadrupole splitting \(\Delta E_Q \approx 40\) mm/s was only slightly dependent on the ionicity of the bridging bond. We feel justified, therefore, in writing

\[
\Delta E_Q = \Delta E_Q^0 + 4\Delta E_Q^0 \left( \frac{1}{2} \cos^2 \alpha - \frac{1}{2} \right) = 6 \Delta E_Q^0 \cos^2 \alpha,
\]

for the quadrupole splitting, where \(\Delta E_Q^0 = \frac{1}{2} \Delta E_Q \approx 20\) mm/s is the quadrupole splitting due to one Xe–F bond.

The crystal structure determination yields \(\alpha \approx 75^\circ - 81^\circ\), corresponding to \(\Delta E_Q = 2.9 - 8.0\) mm/s. This result is consistent with our experimental value, \(\Delta E_Q = 7.7(2)\) mm/s for XeF\(_4\) and it demonstrates the strong dependence of the electric field gradient on the distortion of the octahedron.

The sensitivity of the quadrupole splitting to the geometry of the hexovalent compounds appears to be illustrated by the change of \(\Delta E_Q\) for the XeF\(_2\) adducts (see Table I). Whereas the change of \(\Delta E_Q\) between XeF\(_4\) and XeF\(_2\)SbF\(_6\) is only about 3\%, it amounts to 58\% between XeF\(_4\) and XeF\(_2\)SbF\(_6\)F\(_4\). Since the crystal structure of the latter compound is not known, we cannot check the validity of the simple model in this case.

The oxyfluoro-species XeOF\(_2\)F\(_5\) and XeOF\(_3\) have different geometries, but they also show reduced a Q.S. For XeOF\(_4\), the crystal structure is known.\(^{17}\) It has the square-pyramidal shape shown in Fig. 6, with F–Xe–O angles \(\alpha \approx 92.4^\circ\) and a short Xe–O bond. Taking the contribution to the quadrupole splitting of the four Xe–F bonds in the basal plane to be

\[
4\Delta E_Q^0 (\frac{1}{2} \cos^2 \alpha - \frac{1}{2}) = -39.8\ mm/s,
\]

and combining this with the experimental result \(|\Delta E_Q| = 18.1\ mm/s\),

\[
|\Delta E_Q| \approx (39.8 \pm 18.1) \ mm/s = 21.7\ mm/s\ or\ 57.9\ mm/s,
\]

is obtained for the contribution of the Xe–O bond. The second value can be discarded since it is much larger than that of two Xe–F bonds. The first value \(|\Delta E_Q| = 21.7\ mm/s\), is not far from that found for the Xe–O bonds in the divalent xenon compounds (\(\Delta E_Q\) of XeF\(_2\) = 18.1–20 mm/s). Its somewhat larger value is consistent with the shorter length of the Xe–O bond in XeOF\(_2\) compared with the length of the bridging Xe–O bond in the divalent compounds.

\[N_aXeO_6\]

In this anion, it has been shown by x-ray crystallography that the xenon is surrounded by a regular octahedron of oxygen atoms, consistent with an \(AX_6\) assignment for the XeO\(_6^+\) ion.\(^{19}\) No quadrupole splitting should therefore be expected and none is found. The linewidth of a Na\(_2\)XeO\(_6\) absorber containing 5.1 mg/cm\(^2\) of \(^{129}\)Xe was determined at liquid helium temperature to be \(W^{(4\%)} = 11.18(22)\ mm/s\) and at liquid nitrogen temperature to be \(W^{(4\%)} = 10.20(18)\ mm/s\). Using the known value of the recoilless fraction at 4 K, \(f_R(4\ K) = 0.47(2)\)\(^\text{20}\) and assuming the recoilless fraction to follow a Debye-Waller factor temperature dependence so that \(f_R(78\ K) = 0.18\), we can extrapolate the linewidth to zero effective absorber thickness \(t = f_A n \sigma_A\) (\(n = \text{number of }^{129}\text{Xe atoms/cm}^2, \sigma_A = \text{resonant absorption cross section of } 39.6\text{ keV level}\), assuming the usual linear dependence of \(W_{\text{res}}\) on \(t\). We find \(W_{\text{res}} = 9.6(3)\ mm/s\). This value does not differ significantly from that found for most other absorbers, so it may be concluded that there is no significant residual quadrupole splitting in the absorber.

\[\text{FIG. 6. XeOF}_2\text{ molecule according to Ref. 17.}\]
CONCLUSIONS

Mössbauer spectroscopy of a large number of xenon compounds reveals a quadrupole interaction strength that is the same within a few percent for each Xe–F and Xe–O bond. This results in very similar quadrupole splittings for Xe (II) and Xe (IV) compounds. There is a small increase in splitting with increasing fluorine acceptor strength of groups adducted to XeF₂ and XeF₄, and a small reduction in splitting for Xe–O– bonds compared with Xe–F bonds.

In the Xe (VI) compounds, where both negative and positive contributions to the quadrupole interaction occur, the splittings are generally much smaller and depend strongly on the distortion of the octahedral environment surrounding the xenon atom. A simple model accounts for this effect.

A sharp distinction between the Xe (II), Xe (IV) compounds on the one hand and the Xe (VI) compounds on the other hand is obtained from Mössbauer spectroscopy. The distinction between the Xe (II) and the Xe (IV) compounds, however, is minimal. This is due to the fact that (i) the two line quadrupole spectrum does not depend on the sign of the quadrupole interaction which should be opposite for these two oxidation states and (ii) the isomer shift results are not sufficiently accurate.

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Since the change in nuclear radius between ground state and excited state is positive, such a shift corresponds to an increase of contact density.


8(a) R. J. Gillespie and D. Landa, Inorg. Chem. 12, 1383 (1973); (b) D. E. McKee, A. Zalkin and N. Bartlett, ibid., 12, 1713 (1973).


