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Mössbauer study of rare-gas-matrix isolated ^{125}Te dimers, $^{125}TeF_6$, and $^{125}TeCl_4$ molecules*

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The Mössbauer absorption spectra of $^{125}TeF_6$, $^{125}TeCl_4$, and $^{125}Te_2$ molecules isolated in rare-gas matrices have been measured at 4.2 K. The matrix-isolated TeF_6, $TeCl_4$, and Te_2 molecules have isomer shifts of $-(1.54\pm0.05)$, (1.0 ± 0.1), and $+(0.34\pm0.07)$ mm/sec relative to the Cu-^{125}Sb source, respectively. The Te_2 spectrum shows a quadrupole splitting (QS) of 9.60 ± 0.07 mm/sec, which contains a small asymmetry that is interpreted as an anisotropy in the Debye-Waller factor. Matrix-isolated $TeCl_4$ shows an unresolved QS of 3.5 ± 0.1 mm/sec. Results of Dirac-Fock calculations of electron densities at the nucleus in free atoms and ions of tellurium are given. These densities are combined with the measured isomer shifts to calculate the change in the mean-square nuclear-charge radius, $\Delta\langle r^2\rangle$. Values ranging from $\Delta\langle r^2\rangle=(2.0\pm0.4)\times10^{-3}$ fm^2 to $\Delta\langle r^2\rangle=(3.4\pm0.7)\times10^{-3}$ fm^2 result depending on the assumption of the electron configuration of tellurium in TeF_6.

I. INTRODUCTION

Rare-gas-matrix isolated (RGMI) atoms in neutral and charged states have been studied in the last twenty years by optical-absorption[1] and -emission[2] spectroscopy and electron-paramagnetic resonance.[3] These experiments indicate that the atoms trapped in the rare-gas matrix have properties very similar to those of the free atoms. The first successful rare-gas-matrix isolation Mössbauer experiment was carried out with iodine molecules (I_2) imbedded in a solid argon matrix at 22 K.[4] The first results of a Mössbauer experiment with ^{57}Fe in an argon matrix at 4.2 K were reported by Barrett and McNab[5] and a further study of Fe monomers in Ar, Kr, and Xe was carried out by McNab, Micklitz, and Barrett.[6] Tin atoms were also successfully isolated in a rare-gas matrix and the Mössbauer spectrum of ^{119}Sn was observed.[7]

This paper reports experiments in which the Mössbauer effect of $^{125}Te_2$ is observed in rare-gas matrices of argon and krypton. $^{125}TeF_6$ and $TeCl_4$ molecules were also isolated in a solid argon matrix. The quadrupole splitting (QS) and isomer shift (IS) for the isolated Te dimer TeF_6 and $TeCl_4$ molecules were measured. The IS measurements are discussed using Dirac-Fock relativistic electron density calculations for free atoms and ions.

II. EXPERIMENTAL PROCEDURES

The samples are made in a liquid-helium cryostat, evacuated to a pressure below 10^{-7} Torr. For the TeF_6 experiments a mixture of Ar gas and TeF_6 was made with an Ar-to-TeF_6 ratio of 90 ± 5 (in the remainder of this article we shall use the following notation for the matrix host-to-impurity ratio: $Ar/TeF_6=90\pm5$). The gas enters the cryostat through an adjustable needle valve and escapes from a tube at a distance of ~6 cm from the depositing surface. The rare-gas–TeF_6 mixture condenses on a cooled beryllium disk which is thermally bonded to the bottom of the liquid-helium container. $TeCl_4$ was evaporated from an 8 cm long quartz crucible which was completely covered by Cu foil. The bottom of the crucible was heated to 200 °C and the outlet of the crucible was around 90 °C. These were found to be the best conditions for deposition of a relatively good sample and not having too much condensation at the cool end of the crucible. The open end of the crucible was 3 cm from the depositing surface (Be). The $TeCl_4$ deposition rate was calibrated by a separate experiment by measuring the attenuation of the 6 keV iron x-ray. Ar was used as a matrix and it was deposited in the same configuration as for the Ar-TeF_6 experiment. The Te_2 experiments were carried out by evaporating Te metal (95% enriched in ^{125}Te) from an alumina crucible inserted in a resistance-heated tantalum furnace. The furnace temperature was measured using a Chromel-Alumel thermocouple; the typical operating temperature was about 395 °C. The tellurium deposition rate was calculated using the deposition efficiency of the system (determined in a separate experiment) and by weighting the crucible before and after the experiment. The rare-gas deposition rate was continuously monitored by measuring the attenuation by the rare-gas of the 35.5 keV

γ ray from a Cu-^{125}Sb source.

The Mössbauer spectra were obtained with a conventional constant-acceleration spectrometer. On one end of the velocity transducer was a Cu-^{125}Sb source[8] cooled down to 4.2 K and at a distance of ~2.5 cm from the absorber. On the other end, a Pd-^{57}Co source at room temperature was used for velocity calibration. The 5.8 keV escape peak of a Xe-filled proportional counter was used for detection purposes.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Ar-TeF$_6$

The Mössbauer spectrum of ^{125}TeF$_6$ in solid argon (Ar/TeF$_6$ = 90 ± 5) at 4.2 K shows a single line with a linewidth of 5.98 ± 0.05 mm/sec (Fig. 1). This linewidth is larger than the natural linewidth (4.9 mm/sec), but is typical of single line ^{125}Te absorbers.[8] A large negative IS of −1.54 ± 0.05 mm/sec referred to a Cu-^{125}Sb source at 4.2 K was observed. The Mössbauer spectrum of pure solid TeF$_6$ (thickness: 3.38 mg/cm^2 ^{125}Te) deposited on a cold surface at liquid-helium temperature was also obtained. An IS of −1.64 ± 0.05 mm/sec with respect to Cu-^{125}Sb was observed; within experimental error this IS is equal to the one observed for RGMI TeF$_6$. This is not unexpected since TeF$_6$ is a strongly bonded molecule and, as a solid, it forms a molecular crystal.

B. Te$_2$

The ratios of rare gas to tellurium in the samples studied were Ar/Te$_2 \simeq$ 500 ± 20 and Kr/Te$_2$ $\simeq$ 180 ± 10. In Fig. 2 the Mössbauer spectrum of Kr-Te$_2$ is shown. The main feature of this spec- is the appearance of a well-resolved QS of 9.55 ± 0.05 mm/sec with an IS of +0.31 ± 0.05 mm/sec (referred to Cu-^{125}Sb). For Ar-Te$_2$ a similar spectrum gives a QS of 9.64 ± 0.05 mm/sec and IS of +0.38 ± 0.05 mm/sec. These results are consistent with the assumption that the distance between the Te atoms in the dimer is the same is krypton and argon. This assumption should be correct if the Te–Te bond is much stronger than the Te$_2$ host bond.

The results of a computer fit to the Kr-Te$_2$ and Ar-Te$_2$ spectra using Lorentzian line shapes reveal an asymmetry between the areas of the two lines in each spectrum. In what follows we define the asymmetry (A) as the ratio of the area of the low-energy line (most negative velocity) to the area of the high-energy line (most positive velocity). We find $A = 1.03 \pm 0.02$ for Ar-Te$_2$ and $A = 1.07 \pm 0.04$ for Kr-Te$_2$. This asymmetry indicates the presence of an anisotropy of the atomic vibrations with respect to the molecular axis. The asymmetry in pure tellurium metal has been measured in powdered samples and a value of 1.05 was obtained.[9] This value is in the range of the anisotropy we observe in the tellurium dimers. For a crystal with axial symmetry Kagan[10] showed that the Mössbauer fraction can be written in the form

$$f = \exp[-k_\gamma^2(\langle x_\parallel^2\rangle - \langle x_\perp^2\rangle)\cos^2\varphi - k_\gamma^2\langle x_\perp^2\rangle], \tag{1}$$

where $\langle x_\parallel^2\rangle$ and $\langle x_\perp^2\rangle$ are the mean squares of the projection of the amplitude of vibration of the absorbing nucleus along the symmetry axis and perpendicular to it, k_γ is the wave number of the Mössbauer radiation. The asymmetry for thin absorbers has been evaluated by Karyagin.[11] The values of A vs $\epsilon = k_\gamma^2(\langle x_\parallel^2\rangle - \langle x_\perp^2\rangle)$ were calculated by Flinn *et al.*[12] Using Flinn's calculation we obtain $\epsilon = k_\gamma^2(\langle x_\parallel^2\rangle - \langle x_\perp^2\rangle) \simeq \pm 0.2$ for Kr and $\epsilon = \pm 0.5$ for Ar. The sign can be obtained by comparing with the results for tellurium metal and also by the assumption $\langle x_\parallel^2\rangle > \langle x_\perp^2\rangle$. Thus $\epsilon > 0$ for both Kr and Ar. This

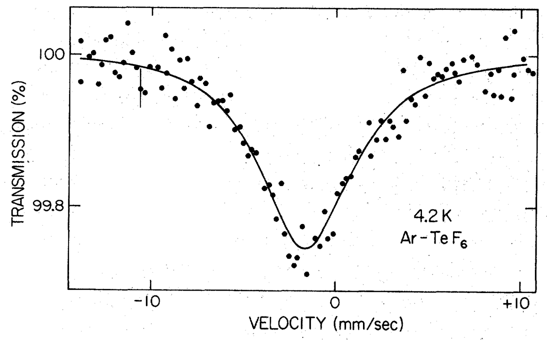

FIG. 1. Mössbauer absorption spectrum of ^{125}TeF$_6$ in an argon matrix, Ar/TeF$_6$ = 90 ± 5, 530 μg/cm^2 ^{125}Te. Doppler velocity referred to Cu-^{125}Sb source at 4.2 K.

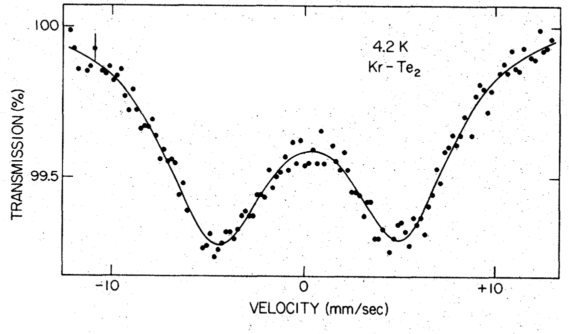

FIG. 2. Mössbauer absorption spectrum of ^{125}Te$_2$ in a krypton matrix, Kr/Te$_2$ = 180 ± 10, 1000 μg/cm^2 ^{125}Te. Doppler velocity referred to Cu-^{125}Sb source at 4.2 K.

means that the transition $\pm\frac{1}{2}\rightarrow\pm\frac{1}{2}$ is lower in energy than the transition $\pm\frac{3}{2}\rightarrow\pm\frac{1}{2}$, i.e., $e^2qQ>0$. Since the quadrupole moment Q of the ^{125}Te nucleus for the $I=\frac{3}{2}$ level is negative,[13] the electric field gradient (EFG) eq must be negative.

The major contribution to the EFG in the Te dimers is expected to come from the aspherical electronic charge density around the ^{125}Te nucleus arising from the unbalanced p valence electrons. The number of electrons in the p_x and p_y orbitals (N_x and N_y) is the same for axial symmetry, i.e., $N_x=N_y$. In this case there are two possibilities for the occupation of the different p orbitals with the four 5p electrons: (a) $N_x=N_y=1$, $N_z=2$ (i.e., σ and π bonding) with $eq=-\frac{4}{5}e\langle 1/r^3\rangle$ or (b) $N_x=N_y=2$, $N_z=0$ (i.e., pure π bonding) with $eq=+\frac{8}{5}e\langle 1/r^3\rangle$. The sign of the EFG determined from the asymmetry in the quadrupole doublet is negative, therefore, (a) gives the occupation of the different 5p orbitals. Since Te_2 is a bound molecule, a mixed σ and π bonding seems more reasonable than the much weaker pure π bonding. For atomic tellurium $\langle 1/r^3\rangle=15.0$ a.u. according to Barnes and Smith.[14] Taking $Q=-0.20\pm0.03$[15] we calculate $\frac{1}{2}e^2qQ=-9.9\pm1.5$ mm/sec. This value agrees, within the experimental error in Q, with our measurement. Boolchand[16] has plotted the QS vs R^{-3} (where R represents the length of Te-host covalent bond) for isoelectronic hosts S, Se, and Te. From our QS of Te_2 and this plot we obtain a value of $R=2.65$ Å for the Te_2 bond length. This value is not far from twice the covalent radius of tellurium (2.72 Å).

C. Ar-TeCl$_4$

The Mössbauer spectrum of $^{125}TeCl_4$ molecules isolated in solid argon ($Ar/TeCl_4=50\pm10$) at 4.2 K shows an unresolved quadrupole doublet (Fig. 3). The solid line in Fig. 3 is the computer fit of the spectrum assuming Lorentzian line shapes. From the fit, the values of the QS and IS were, respectively, 3.5 ± 0.1 mm/sec and 1.0 ± 0.1 mm/sec. The Mössbauer spectrum was also obtained for a pure solid $TeCl_4$ absorber (4.6 mg/cm^2 of ^{125}Te). The value for the QS was 3.45 ± 0.1 mm/sec and the IS was 0.74 ± 0.1 mm/sec. One observes that there is no significant difference in the QS between the pure solid and the matrix isolated $TeCl_4$, but that there is a small difference (~0.3 mm/sec) in the IS between the pure solid and the Ar-$TeCl_4$ absorbers. This could be related to the observed difference in the structure between $TeCl_4$ in the gas phase, where electron-diffraction measurements[17] show a bipyramid structure, and the solid, where infrared[18] and Raman[19] measurements suggest for the $TeCl_4$ compound an ionic structure $TeCL_3^+Cl^-$ with a local symmetry C_{3v}. Solid $TeCl_4$ crystallizes into a monoclinic structure and, due to the low symmetry, one would expect a difference in the QS between the RGMI $TeCl_4$ and the pure solid. That is not what is observed. This suggests that the EFG is produced only by the ligands and is independent of the local symmetry. In the following paragraph we will analyze the IS results assuming a pure ionic configuration $[\mathrm{Kr}]4d^{10}5s^2$ for $TeCl_4$ since no self-consistent Hartree-Fock (SCHF) cluster calculations for this compound are available.

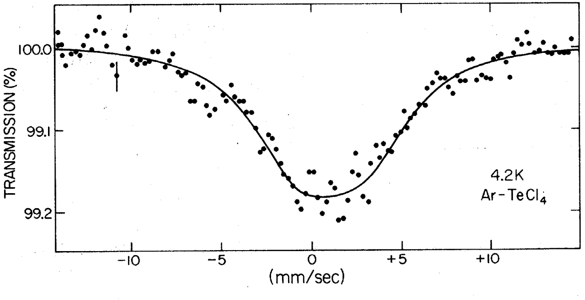

FIG. 3. Mössbauer absorption spectrum of $^{125}TeCl_4$ in an argon matrix, $Ar/TeCl_4=60\pm10$, 700 μg/cm^2 ^{125}Te. Doppler velocity referred to Cu-^{125}Sb source at 4.2 K.

D. Isomer shifts

The Mössbauer isomer shift is given by[20]

$$\delta V_{\mathrm{IS}}=6.105\,(Z/E_\gamma)\,\Delta\langle r^2\rangle\,\Delta\rho(0)\ , \qquad (2)$$

where δV_{IS} is the isomer shift in mm/sec, $\Delta\langle r^2\rangle$ is the change in mean-square nuclear radius $\Delta\langle r^2\rangle=\langle r^2\rangle_{\mathrm{excited}}-\langle r^2\rangle_{\mathrm{ground}}$ and is given in units of fm^2, $\Delta\rho(0)$ is the difference between electron densities at the nucleus (in units of a_0^{-3}), E_γ is the transition energy in keV, and Z is the atomic number. Sometimes the nuclear parameter used is $\delta R/R$, where R is the nuclear charge equivalent radius ($R=1.2A^{1/3}$ fm) and δR is the change in the charge radius between the excited and ground state of the nucleus, the intercomparison is $R^2(\delta R/R)=\frac{5}{6}\Delta\langle r^2\rangle$.

There is a difficulty in correlating isomer-shift data and electron densities at the nucleus. This arises from the uncertainty in the application of free-atom or free-ion wave functions to solids and in the choice of electron configurations for particular reference compounds. The matrix-isolation technique with atoms and ions has provided the possibility of obtaining IS values for Mössbauer nuclei where the free-atom or -ion calculation can be applied.

In the case of matrix-isolated molecules, self-consistent cluster calculations[21] would be needed in order to correlate such isomer-shift data with electron densities at the nucleus. Since such calculations are not available for TeF_6, $TeCl_4$, and

TABLE I. Values of electron density at the nucleus for some electronic configurations of tellurium. The electron densities were evaluated using Dirac-Fock calculations.

Atomic configuration	$\rho(0)(a_0^{-3})$
$[\mathrm{Kr}]4d^{10}5s^2 5p^4$	228 239.22
$4d^{10}5s^2 5p_{1/2}^2$	228 257.95
$4d^{10}5s\,5p_{1/2}^2 5p_{3/2}$	228 194.97
$4d^{10}5s^2$	228 279.31
$4d^{10}$	228 134.15

Te_2 we have used Dirac-Fock wave functions to calculate the electron densities at the Te nucleus for different Te configurations. We have taken for the nuclear charge radial distribution $d(r) = d_0[1+e^{(r-c)/a}]^{-1}$ with $c = 5.39$ fm and $a = 0.55$ fm. The results are given in Table I. These calculations are plotted in Fig. 4 with the RGMI isomer shifts measured for the Te_2, $TeCl_4$, and TeF_6. We have used the electron density of the free atom to describe the Te dimer. This is not entirely correct since there are bonding effects present in Te_2. However, since the removal of one $5p$ electron from the monomer would increase the electron density $\Delta\rho(0)$ to approximately 116 (see Table I), the neglecting of bonding effects introduces only a relatively small error.

More difficult is the evaluation of the electron density at the Te nucleus in TeF_6. If TeF_6 was a completely ionic compound, the Te electron configuration would be $[\mathrm{Kr}]4d^{10}$; on the other hand, the configuration $5s5p^3 5d^2$ is predicted for Te in TeF_6 from the point of view of coordination chemistry.[22] The two Te configurations give lower and upper limits for the electron density in TeF_6. A similar, but smaller uncertainty, exists for $TeCl_4$. The $\rho(0)$ for the configuration $[\mathrm{Kr}]4d^{10}5s^2$ will be a good approximation for Te in $TeCl_4$ because of the the ionic character of this compound. Using the IS values of TeF_6 RGMI and $TeCl_4$ RGMI and the configurations $4d^{10}$ for TeF_6 and $4d^{10}5s^2$ for $TeCl_4$, one obtains $\Delta\langle r^2\rangle = (2.0 \pm 0.4) \times 10^{-3}$ fm^2 ($\delta R/R = 6.5 \times 10^{-5}$); using the $5s5p^3$ configuration for TeF_6 ($5s5p^3$ and $5s5p^3 5d^2$ give nearly the same density at the nucleus), one obtains $\Delta\langle r^2\rangle = (3.4 \pm 0.7) \times 10^{-3}$ fm^2 ($\delta R/R = 11.3 \times 10^{-5}$). These $\Delta\langle r^2\rangle$ values give a lower and upper limit for $\Delta\langle r^2\rangle$ in ^{125}Te. The value of $\Delta\langle r^2\rangle$ obtained by comparing isoelectronic compounds[23] is 2.7×10^{-3} fm^2 and is within the range of our results.

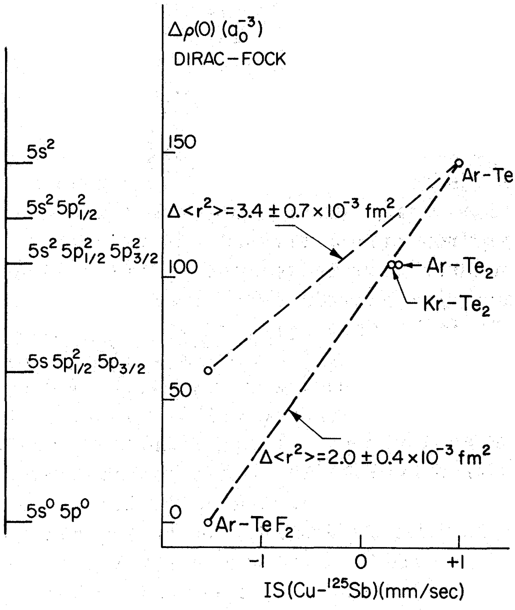

FIG. 4. Correlation between electron density differences $\Delta\rho(0)$ at the nucleus and the IS for ^{125}Te. IS values are given relative to a Cu-^{125}Sb source at 4.2 K. Electron densities were calculated using Dirac-Fock wave functions.

IV. CONCLUSION

Te dimers TeF_6 and $TeCl_4$ have been successfully isolated in rare-gas matrices. An anisotropy of the Debye-Waller factor has been detected in the Te_2 dimer. Using Dirac-Fock calculations for free atoms and ions and the values of the IS for the matrix isolated TeF_6, Te_2, and $TeCl_4$ a range of values for $\Delta\langle r^2\rangle$ is given. Self-consistent cluster calculations of these Te compounds are needed for a more accurate IS calibration for ^{125}Te.

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