

Mössbauer study of pure H_2Te and photodissociated H_2Te in argon*

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The Mössbauer spectrum of solid H_2Te was observed at 4.2 K and gave a quadrupole splitting (QS) of 7.2 ± 0.2 mm/sec and an isomer shift (IS) of -0.1 ± 0.2 mm/sec relative to a $\text{Cu-}^{125}\text{Sb}$ source. The Mössbauer spectrum of photodissociated H_2Te in solid argon is proposed as that of Te atoms. It shows a QS of 9.2 ± 0.2 mm/sec and an IS of 0.0 ± 0.2 mm/sec relative to a $\text{Cu-}^{125}\text{Sb}$ source. The IS values of Te^0 were combined with those of argon matrix isolated $^{125}\text{TeCl}_4$ (1.0 ± 0.1 mm/sec) and the results of Dirac-Fock electron-density calculations to give $\Delta\langle r^2 \rangle = (2.8 \pm 0.5) \times 10^{-3} \text{ fm}^2$ for the 35.5-keV level in ^{125}Te .

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 emission spectroscopy,² electron paramagnetic resonance,³ and the Mössbauer effect.⁴ These experiments indicate that the atoms and molecules trapped in the rare-gas-matrix have properties very similar to those of the free species, demonstrating that the weak binding in these solids does not change appreciably the atomic and molecular configuration. In a recent work, tellurium molecules were isolated in rare-gas solids and the isomer shifts (IS) were analyzed using Dirac-Fock relativistic electron-density calculations for free atoms and ions.⁵ The densities were combined with the IS to calculate the change in the mean-square nuclear-charge radius $\Delta\langle r^2 \rangle$. Values ranging from $\Delta\langle r^2 \rangle = (2.0 \pm 0.4) \times 10^{-3} \text{ fm}^2$ to $\Delta\langle r^2 \rangle = (3.4 \pm 0.7) \times 10^{-3} \text{ fm}^2$ were obtained.

In this paper we report the observation of the Mössbauer effect in the molecular solid H_2Te .^{6,7} Because of failures to obtain Te monomer from the metal vapor, we have investigated the possibility of producing the monomer by the dissociation of Te molecules. This type of experimental technique has been widely applied in matrix-isolation work when the production of the desired species from the vapor was not feasible.⁸ We found the highly unstable molecules H_2Te to be the most appropriate for this purpose. We photodissociated the above molecule isolated in solid argon, and identified the observed Mössbauer spectrum as that of the monomer. From the IS of the Te monomer in argon and using Dirac-Fock relativistic electron-density calculations for the free atom, a more accurate value of $\Delta\langle r^2 \rangle$ is given.

II. EXPERIMENTAL TECHNIQUE

The samples are made in a liquid-helium cryostat, evacuated to a pressure below 10^{-7} Torr. The Mössbauer spectra were obtained with a conventional constant-acceleration spectrometer. On one end of the velocity transducer was a ($\text{Cu-}^{125}\text{Sb}$) source cooled down to 4.2 K and at a distance of ~ 2.5 cm from the absorber. On the other end, a ($\text{Pd-}^{57}\text{Co}$) 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.

Hydrogen telluride can be prepared by the action of water or hydrochloric acid on aluminum telluride; using 4N HCl, a yield of 80% H_2Te can be obtained.⁷ After several tests it was decided to use the reaction of Al_2Te_3 and HCl as the source of H_2Te . Two stainless-steel containers were used for the production of H_2Te . They were connected through a valve to the cryostat. Hydrochloric acid solidified at 77 K was introduced into a container partially filled with Al_2Te_3 (20% more HCl than required by stoichiometry). The handling of the substances was carried out in an inert atmosphere. This container was sealed, cooled to 77 K, and pumped to a vacuum better than 10^{-6} Torr. Then the container was warmed up to a temperature where the HCl melted and H_2Te is a gas (melting point, 221.8 K; boiling point, 271 K). Al_2Te_3 and HCl reacted and H_2Te was produced and collected in the other container, which was previously evacuated. This second container was subsequently isolated from the first container and maintained at a temperature of 223 K. Some contamination with water in the container is still possible in our experiment; however, there is not enough to dissociate all the H_2Te . The deposition for a pure- H_2Te sample was carried out at a con-

tainer temperature of 223 K. The deposition rate of the H_2Te was calculated from the attenuation by the sample of the 6-keV x ray of a ^{57}Co source. The sample was deposited onto a Be disk at 78 K. The system was light tight so that no photodissociation could occur. The above experiment was repeated several times; it was observed that 90% of the H_2Te was deposited in the first half hour. Figure 1 shows a typical Mössbauer spectrum of H_2Te at 4.2 K.

The photodissociation of H_2Te was produced by irradiating a sample of H_2Te molecules isolated in a solid argon matrix. Argon and H_2Te were codeposited onto a sapphire disk held at about 5 K. The H_2Te gas temperature was increased to 260 K for this experiment. At this temperature there is partial dissociation of the H_2Te . The sample was irradiated during deposition and for 6 h after deposition by a tungsten lamp. The atomic ratio of rare gas to tellurium in the sample studied was 62 ± 5 . The above experiment was repeated with a similar atomic concentration, but instead of irradiating with a standard tungsten lamp, uv radiation from a xenon lamp was used (2500–3100 Å).

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

H_2Te : The Mössbauer spectrum of H_2Te at 4.2 K is shown in Fig. 1. The spectrum shows a quadrupole splitting (QS) of 7.2 ± 0.2 mm/sec and an IS of -0.1 ± 0.2 mm/sec (with respect to a $\text{Cu-}^{125}\text{Sb}$ source). The linewidth is 5.0 ± 0.2 mm/sec. The presence of a QS indicates that the symmetry of solid H_2Te at 4.2 K is lower than cubic. The

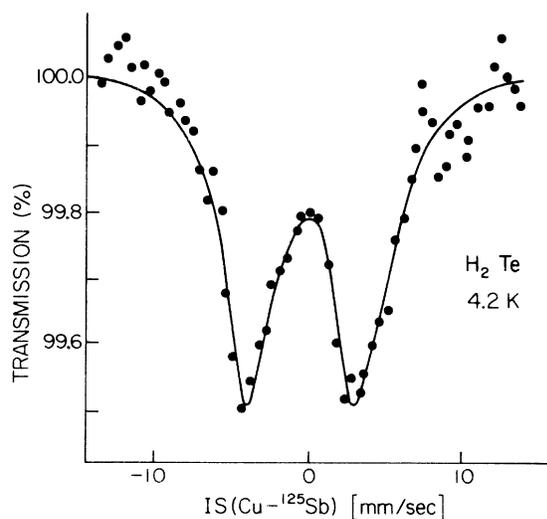


FIG. 1. Mössbauer absorption spectrum of H_2Te at 4.2 K ($600\text{-}\mu\text{g}/\text{cm}^2$ ^{125}Te). Doppler velocity is referred to a $\text{Cu-}^{125}\text{Sb}$ source at 4.2 K.

isomorphous molecular crystals H_2Se and H_2S are cubic, but H_2S has a stable tetragonal form below 103 K.⁹ No crystallographic information is available on H_2Te , but from the Mössbauer spectrum a tetragonal lattice at 4.2 K is the most probable. If the H_2Te compound were ionic one would expect the Te to be in a Te^{2-} state, in which case the ion would be an s state and no QS due to the valence electrons is expected. Such a situation has been observed by Boolchand¹⁰ in Li_2Te , in which case there is no QS and the IS is -0.53 mm/sec (with respect to $\text{Cu-}^{125}\text{Sb}$). By contrast, the IS of H_2Te is different from Li_2Te indicating a different electronic configuration, moreover, an appreciable QS is observed. The electronegativities of tellurium and hydrogen are equal,¹¹ but Li is less electronegative than tellurium. For example, in LiH the electron concentration is higher around the hydrogen than around the lithium¹¹ indicating a high degree of ionicity. A similar situation should exist in Li_2Te . In the case of H_2Te one expects that the tellurium atomic configuration will not be far from the neutral state. Indeed, the above statement is in agreement with the upper limit of 0.2 D for the dipole moment of H_2Te .¹¹ The tellurium-hydrogen bond length has been estimated at 1.7 Å, and the angle H–Te–H at $89^\circ 30'$.¹² The QS observed in solid H_2Te is smaller than predicted for such a bond angle in the case of bonds formed with pure p orbitals.¹³ This QS is not completely unexpected for H_2Te , since measurements of the quadrupole coupling constants of the H_2S molecule (bond angle $92^\circ 6'$) suggest that the bonding orbitals are spd hybrids.¹⁴ Possible lattice contribution cannot be disregarded either.

After the deposition of the H_2Te -argon sample and before irradiation with a tungsten light source, a Mössbauer spectrum with a QS of 8.9 ± 0.2 mm/sec, and IS of -0.2 ± 0.2 mm/sec, and a linewidth of 5.7 ± 0.2 mm/sec is observed. After 6 h of irradiation a spectrum as shown in Fig. 2 was observed with a QS of 9.2 ± 0.2 mm/sec, and IS of 0.0 ± 0.2 mm/sec, and a linewidth of 5.0 ± 0.2 mm/sec. There is a slight asymmetry in the spectrum, which could be explained by the presence of some tellurium dimers. Since the atomic ratio Ar to Te is ≈ 62 , there is about 10% probability of having Te-Te nearest neighbors. We interpret the preirradiation spectrum as produced by a mixture of H_2Te and Te monomers, the monomer being produced by dissociation in the H_2Te gas and photodissociation of H_2Te by room light entering the cryostat during deposition. The postirradiation spectrum with its narrower linewidth is interpreted as being produced primarily by Te monomers. One can disregard recombination of Te atoms with hydrogen in the matrix because of

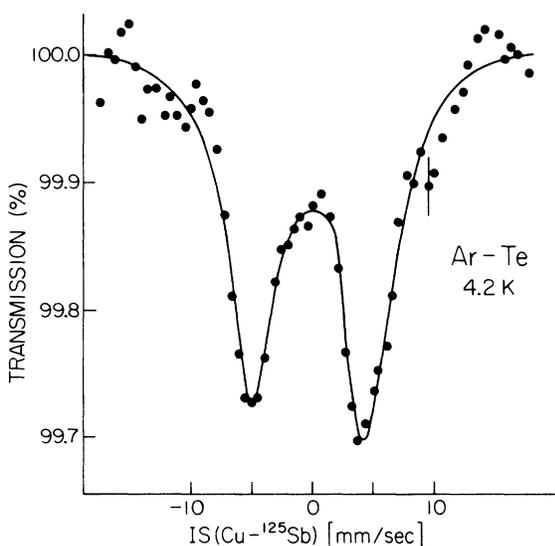


FIG. 2. Mössbauer absorption spectrum of Te monomer in an argon matrix. Doppler velocity is referred to a $\text{Cu-}^{125}\text{Sb}$ source at 4.2 K.

the presence of light during all the experiments and the weak bond and instability of H_2Te . It is more probable that hydrogen atoms recombine to form H_2 or combine with impurities and/or diffuse out of the argon matrix. Other molecules that might be produced in the matrix are TeO_2 , TeO_3 , and H_2TeO_3 . The isomer shifts of these molecules do not agree with the values observed in this experiment: TeO_3 (IS: -0.8 mm/sec), TeO_2 (IS: $+0.9$ mm/sec), and H_2TeO_3 (IS: $+1.2$ mm/sec).¹⁵

The above experiment was repeated with similar atomic concentrations, and using uv radiation ($2500\text{--}3100$ Å) from a xenon lamp. Under these circumstances there would be negligible H_2Te left after irradiation. One observes a Mössbauer spectrum with a QS of 9.1 ± 0.2 mm/sec and IS of -0.1 ± 0.2 mm/sec in good agreement with the former measurements.

We propose that the IS and QS of the postirradiation sample are those of the matrix-isolated monomer of tellurium. The basic argument for this assignment is the elimination of other possible molecules: irradiation dissociates H_2Te and the isomer shifts of other possible molecules do not agree with the observed IS. The following analysis assumes this identification of the monomer.

The QS of the Te monomer is less than the one observed for Te dimers.⁵ The EFG at the ^{125}Te nucleus is produced by the splitting of the p levels in the weak noncubic crystal field of the matrix produced by lattice defects resulting from the fast deposition rate. A partial population of the excited p states is possible at 4.2 K, consequently reducing

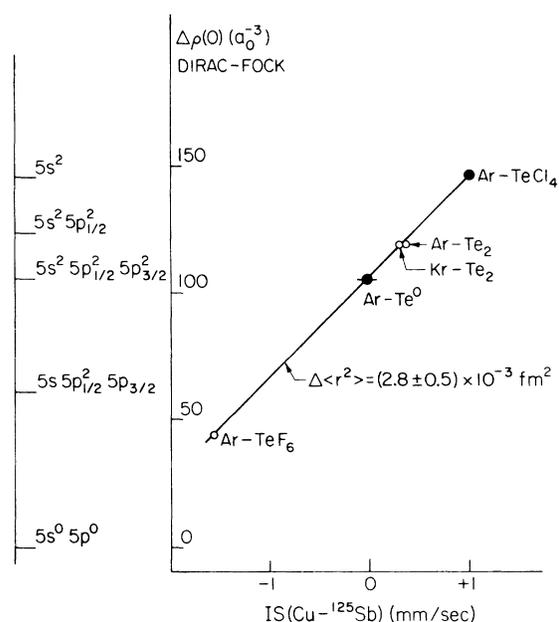


FIG. 3. Correlation between electron density differences $\Delta\rho(0)$ at the nucleus and the IS for ^{125}Te . The IS values are given relative to a $\text{Cu-}^{125}\text{Sb}$ source at 4.2 K. Electron densities were calculated using Dirac-Fock wave functions. The calibration lines was calculated using the IS of Ar-TeCl_4 and Ar-Te (filled circles).

the observed QS.

We will use the IS values for the Te^0 and Te^{4+} to calculate the change in the mean-square nuclear radius $\Delta\langle r^2 \rangle = \langle r^2 \rangle_{\text{excited}} - \langle r^2 \rangle_{\text{ground}}$ for ^{125}Te . The Mössbauer IS is given by¹⁶

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

where δV_{IS} is the IS in mm/sec, $\Delta\rho(0)$ 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 the atomic number. We will use Dirac-Fock wave functions to calculate the electron densities at the Te nucleus for different Te configurations. For these calculations the nuclear charge radial distributor $d(r) = d_0(1 + e^{(r-c)/a})^{-1}$ was used; $c = 5.39$ fm and $a = 0.55$ fm. The isomer shifts of Te^0 , and $^{55}\text{TeCl}_4$ (IS: 1.0 ± 0.1 mm/sec) were used for calculating $\Delta\langle r^2 \rangle$. The $\rho(0)$ for the configuration $(\text{Kr}) 4d^{10}5s^2$ was assumed for Te in TeCl_4 because of the ionic character of this compound. We obtained a value of $\Delta\langle r^2 \rangle = (2.8 \pm 0.5) \times 10^{-3} \text{ fm}^2$. This value is almost identical to the one obtained by comparison of isoelectronic compounds.^{17,18} In Fig. 3 the IS is plotted for the different matrix-isolated tellurium species versus electron density differences. The point for TeF_6 in Fig. 3 is plotted on the line established by TeCl_4 and Te^0 at the value of its IS, -1.54 ± 0.05 mm/

sec.⁵ The electron density for this point is close to that for a sp^3d^2 configuration which is predicted from coordination chemistry arguments for TeF_6 .¹⁸ The point for Te_2 is plotted on the calibration line at the value of its IS. This procedure gives a value for the electron density at the tellurium

nucleus in Te_2 that is slightly larger than for the Te monomer. This indicates that an overlap of the p and s orbitals is taking place in the dimer. For obtaining a more accurate value of $\Delta\langle r^2 \rangle$ self-consistent cluster calculations of Te_2 and TeCl_4 are necessary.

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¹D. M. Mamm and H. P. Broida, *J. Chem. Phys.* **55**, 84 (1971), and references contained therein.

²M. Peyton and H. P. Broida, *J. Chem. Phys.* **30**, 1139 (1959).

³G. S. Jackel, W. H. Nelson, and W. Gordy, *Phys. Rev.* **176**, 453 (1968).

⁴S. Bukshpan, C. Goldstein, and T. Sonnino, *J. Chem. Phys.* **49**, 5477 (1968); P. H. Barrett and T. K. McNab, *Phys. Rev. Lett.* **25**, 1601 (1970).

⁵P. H. Barrett, P. A. Montano, H. Micklitz, and J. B. Mann, *Phys. Rev. B* **12**, 1676 (1975).

⁶*Gmelins Handbuch Der Anorganischen Chemie, Tellur*, edited by Erich Pietsch (Verlag, Berlin, 1940).

⁷*Tellurium*, edited by W. Charles Cooper (Van Nostrand, New York, 1971).

⁸Beat Mayer, *Low Temperature Spectroscopy* (American Elsevier, New York, 1971); P. H. Kasai, *Phys. Rev. Lett.* **21**, 67 (1968).

⁹Ralph W. G. Wyckoff, *Crystal Structure* (Interscience,

New York, 1963), Vol. 1.

¹⁰P. Boolchand (private communication).

¹¹Linus Pauling, *The Nature of the Chemical Bond* (Cornell U.P., Ithaca, N. Y., 1960); C. G. Pimentel and R. D. Spratley, *Chemical Bonding* (Holden-Day, San Francisco, 1969).

¹²K. Rossman and J. W. Straley, *J. Chem. Phys.* **24**, 1276 (1956).

¹³W. Gordy, W. V. Smith, and R. F. Trambarulo, *Micro-wave Spectroscopy* (Wiley, New York, 1953).

¹⁴Charles A. Burrus, Jr. and Walter Gordy, *Phys. Rev.* **92**, 274 (1953).

¹⁵P. Jung and W. Trifthäuser, *Phys. Rev.* **175**, 512 (1968); M. L. Unland, *J. Chem. Phys.* **49**, 4514 (1968).

¹⁶G. M. Kalvius, in *Hyperfine Interaction in Excited Nuclei*, edited by G. Goldring and R. Kalish (Gordon and Breach, New York, 1971), Vol. 2, p. 523.

¹⁷G. M. Kalvius and G. K. Shenoy, *At. Data Nucl. Data Tables* **14**, 639 (1975).

¹⁸S. L. Ruby and G. K. Shenoy, *Phys. Rev.* **186**, 326 (1969).