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He($2\,^3S$) along the reaction tube. On the other hand, difficulties could arise if other excited species such as He($2\,^1S$), $He^+$, or $He_2^+$ were to contribute significantly to the population of the emitting state, for then the intensity would no longer be directly proportional to the concentration of He($2\,^3S$) and the spatial variation of intensity with distance would not follow a simple exponential decay law. Fortunately there is evidence that either the concentration of these other species are very low,[1] or else they contribute weakly to the population of the emitting state.[16] Thus the emission measurements can be compared with the optical absorption experiments, which measure directly the disappearance of He($2\,^3S$). In the atomic beam experiments the reported cross sections refer to the total production of ions by the metastable helium atoms. Agreement between the rate coefficients obtained in this way with those based on the optical measurements can be expected if de-excitation of metastable helium by processes other than Penning ionization are not important.

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# Vibrational Spectra and Structure of Four-Membered Ring Molecules. XIV. Vibrational Analysis and Ring Puckering Vibration of Trimethylene Selenide and Trimethylene Selenide-$d_4$*

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The infrared and Raman spectra of trimethylene selenide (TMSe) and trimethylene selenide-2,2,4,4-$d_4$ (TMSe-$d_4$) have been recorded from 4000 to 15 cm$^{-1}$ in gaseous, liquid, and solid states. A vibrational assignment of the fundamentals is consistent with the expected $C_s$ equilibrium configuration. A series of sharp bands associated with the ring puckering vibration have been observed in the mid- and far-infrared regions. The frequencies of the transitions have been employed in determining the following double-minimum potential, barrier-to-ring inversion, and the equilibrium separation of the ring diagonal, $2x$ in angstroms, for TMSe, respectively: $V(\mathrm{cm}^{-1})=4.258\ (\pm0.02)\times10^5x^4-2.5391\ (\pm0.007)\times10^4x^2$; 378.1±4 cm$^{-1}$; 0.35 Å. For TMSe-$d_4$ these quantities are: $V(\mathrm{cm}^{-1})=3.242(\pm0.1)\times10^5x^4-2.208\ (\pm0.033)\times10^4x^2$; 375±10 cm$^{-1}$; 0.37 Å, respectively. The dihedral angle of both molecules is calculated to be 32.5±2°.

## INTRODUCTION

The ring-puckering vibration in four-membered ring molecules has been of interest for several years.[1–5] This vibration is important because it often provides considerable information relating to the structure of the ring skeleton. Unfortunately, this motion is inactive in the infrared spectrum of cyclobutane, perhaps the most important four-membered ring of all, and it has not been observed in the Raman effect. Therefore, the structure of the molecule was originally sought by the investigation of other four-membered ring compounds which have infrared-active ring-puckering modes. Trimethylene oxide (TMO)[1,2] and trimethylene sulfide (TMS)[3,4] were among the first molecules to be investigated.

As with all four-membered ring compounds, the ring-puckering vibration in trimethylene oxide and sulfide lies in the far-infrared. In both these molecules the vibration appears as a series of very sharp $Q$ branches which are well separated due to high anharmonicity and have high relative intensity due to favorable Boltzmann distributions. From the far-infrared spectra, trimethylene oxide is found to have a planar or nearly planar ring skeleton, whereas TMS is puckered. Each potential function for the ring-puckering vibrations of TMO and TMS contains an important quartic term and a negative harmonic component. The latter provides the necessary maximum at the center of the potential function. In TMO this maximum lies below the ground energy level (and is therefore a nearly pure quartic oscillator), whereas in TMS it is about 273 cm$^{-1}$ in height. Energy-level transitions calculated from such a

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[1] A. Danti, W. J. Lafferty, and R. C. Lord, J. Chem. Phys. **33**, 294 (1960).

[2] S. I. Chan, J. Zinn, J. Fernandez, and W. D. Gwinn, J. Chem. Phys. **33**, 1643 (1960); **34**, 1319 (1961); S. I. Chan, T. R. Borgers, J. W. Russell, H. L. Strauss, and W. D. Gwinn, *ibid.* **44**, 1103 (1966).

[3] J. R. Durig and R. C. Lord, J. Chem. Phys. **45**, 61 (1966).

[4] D. O. Harris, H. W. Harrington, A. C. Luntz, and W. D. Gwinn, J. Chem. Phys. **44**, 3467 (1966).

[5] J. Laane and R. C. Lord, J. Chem. Phys. **47**, 4941 (1967).

simple potential energy scheme are in excellent agreement with the observed far-infrared frequencies.

The equilibrium structure of the ring skeleton in four-membered ring molecules is thought to be the result of a balance between ring strain and torsional repulsion of adjacent methylene groups. The higher barrier in TMS is then attributed to a lessening of ring strain since normal bond angles about analogous acyclic sulfides are much smaller than the corresponding ether molecules. In TMSe there is undoubtedly even less ring strain but, again, nearly unchanged repulsive forces between adjacent methylene groups. Hence, in this case, an even higher barrier can be anticipated with at least two and possibly three pairs of split levels lying below the top of the barrier. These expectations have already been realized[6] by a previous (tentative) assignment of mid- and far-infrared spectra. In this publication we report a confirmation of the previous work from additional data and more refined results. Moreover, a vibrational analysis is presented to further establish the point group symmetry of this molecule.

## EXPERIMENTAL

Although the synthesis of trimethylene selenide has been previously reported,[7] a somewhat different approach was found to be more convenient. By our method, which is similar to a synthesis of the sulfur analog,[8] sodium selenide is formed by reacting sodium metal and elemental selenium in liquid ammonia. The liquid ammonia is then replaced by diethyl ether by allowing the ammonia to boil off as the ether is added dropwise. Redistilled trimethylene dibromide in ether solution is then added dropwise to a slurry of sodium selenide in about 20% excess with rapid stirring. The stirring is continued for 2 h after terminating the addition of the dibromide. At this point the contents of the reaction vessel are filtered and the filtrate is distilled on a Vigreux column. After removal of the ether fraction, the product is obtained under reduced pressure as a slightly yellow liquid with a pungent odor. NMR[9] and mass spectra confirm the presence of the compound with only trace impurities which may impart the yellow color. TMSe-$d_4$ was obtained by replacing the trimethylene dibromide with $BrCD_2CH_2CD_2Br$ which was purchased from Merck, Sharp, and Dohme of Canada. It is estimated that deuteration on the $\alpha$-carbon atoms is better than 98%. It appears that trimethylene selenide is fairly stable if stored in a cool, dark place and in the presence of air. However, whenever a liquid sample of the compound is degassed, polymerization immediately sets in and within an hour the monomer has almost completely reacted.

Mid-infrared spectra were recorded on a Beckman IR-11 and on an RIIC FS-520 Fourier interferometer equipped with 7 m of light pipe which served both as a gas cell and a radiation conduit to the gallium-doped germanium detector cooled by liquid helium. The deep far-infrared region ($<50$ cm$^{-1}$) was examined with an indium antimonide detector. Infrared spectra of the vaporous materials taken on the grating instruments were recorded at vapor pressures up to 15 torr in a sample cell of variable path length up to 10 m. Spectra of the samples in the solid state were obtained from films of unknown thickness produced by condensing the gaseous compounds on a CsI substrate cooled by liquid nitrogen. In one experiment the vapor was diluted with argon and deposited at liquid-hydrogen temperatures. It should be mentioned that when trimethylene selenide is annealed at its melting point, very rapid polymerization takes place. A study of this process will be reported in a subsequent publication.[10]

Raman spectra were recorded on a Cary 81 spectrophotometer equipped with an He–Ne laser. The samples were examined in Pyrex "melting-point" capillary tubes by means of axial excitation. Hence, polarization measurements are considered crude at best. Nonetheless, such data are useful for establishing the totally symmetric vibrations which result in strongly polarized lines. Depolarized lines were tentatively identified by comparing the depolarization factor of the line with one known to be nontotally symmetric by other means, e.g., infrared gas-phase band contours.

### Assignment of the Fundamentals

As has been shown earlier,[6] trimethylene selenide is puckered with $C_s$ symmetry, the symmetry plane passing through the selenium atom and the atoms of the $\beta$-methylene group. Hence, its 24 normal modes, all active in both the infrared and Raman, are divided into 14 symmetric $A'$ vibrations and 10 antisymmetric $A''$ vibrations. As in TMO and TMS the $C$ axis lies in the symmetry plane, passes through the ring, and is perpendicular to what would be the molecular plane in the planar configuration. The axis of smallest inertia lies in the symmetry plane while the axis of intermediate inertia lies perpendicular to the plane. Therefore, normal modes which have oscillating dipole moments that lie in the symmetry plane will have type-$A$, type-$C$, or hybrid band types and are classified as totally symmetric ($A'$) vibrations. Type-$B$ bands arise when the direction of the dipole-moment derivative of the normal vibration lies perpendicular to the symmetry plane. Such vibrations are classified as nontotally symmetric ($A''$).

The mid-infrared spectra of TMSe (and TMSe-$d_4$) in the vapor and solid phases appear in Figs. 1 and 2, respectively. The Raman spectra of the two species are illustrated in Fig. 3. Table I contains the assignment of the normal vibrations and the discussion of the assign-

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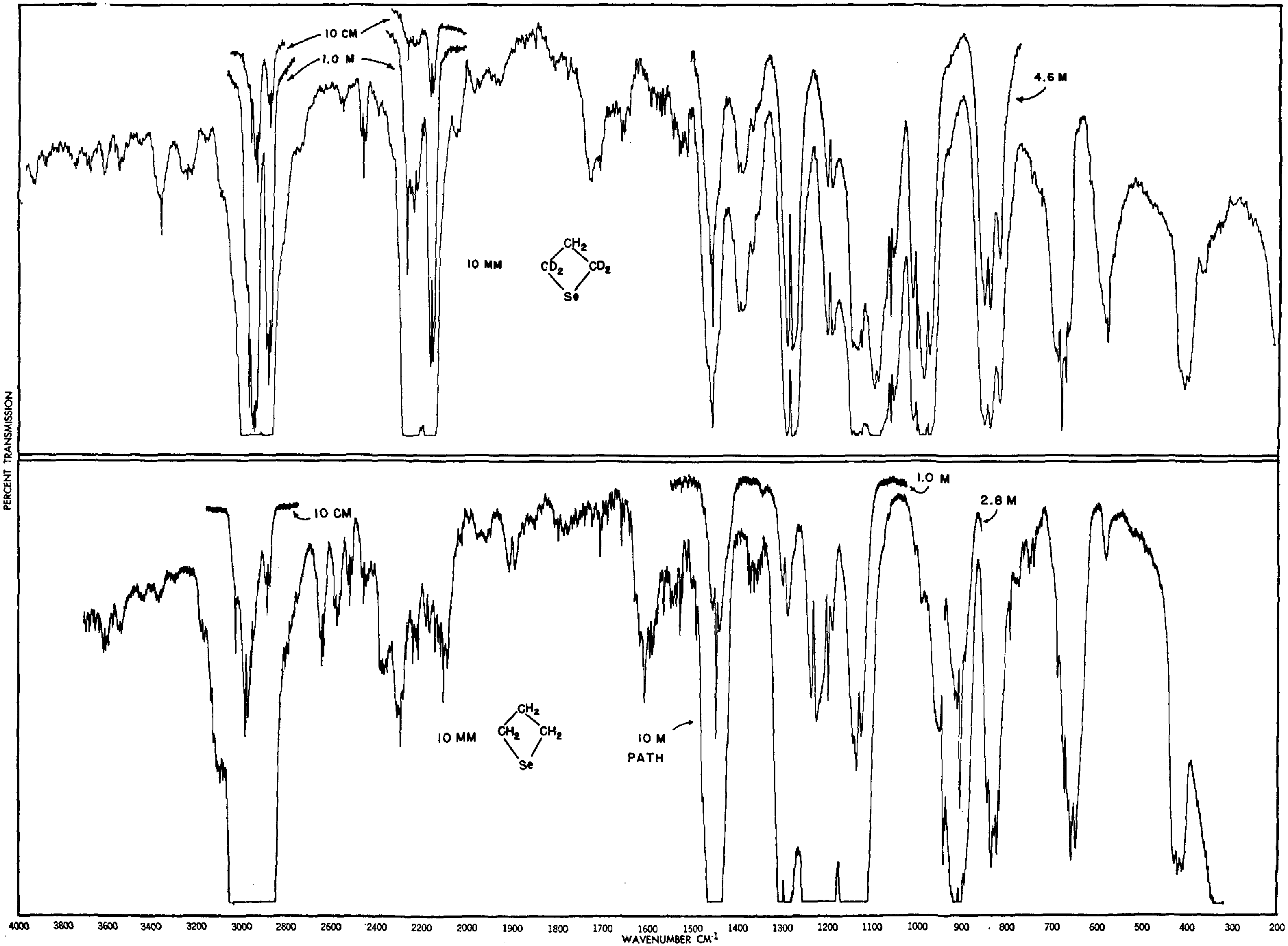

FIG. 1. The mid-infrared spectra of trimethylene selenide and trimethylene selenide-$d_4$ vapors at various path lengths.

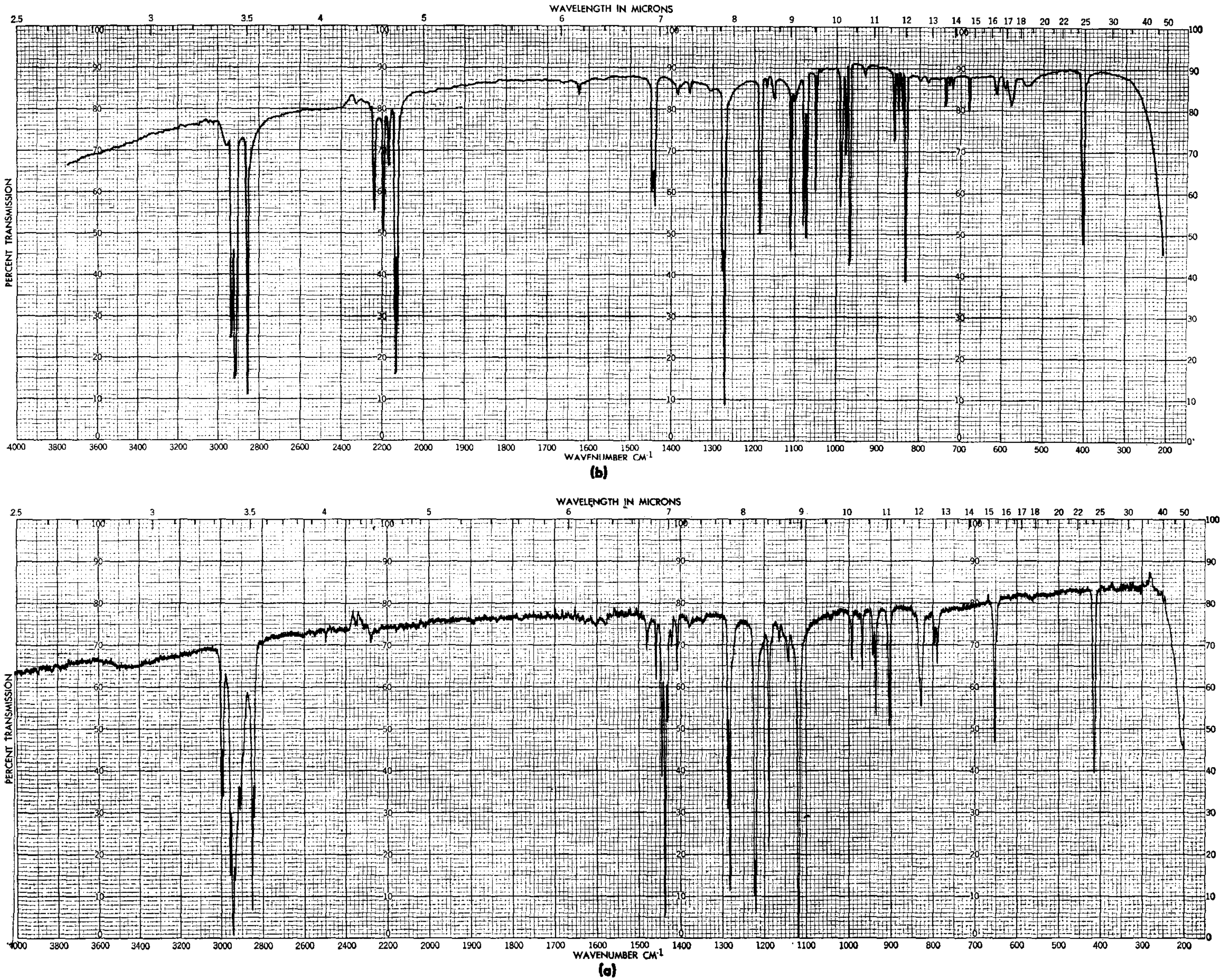

FIG. 2. The mid-infrared spectra of polycrystalline trimethylene selenide (a) and trimethylene selenide-$d_4$ (b) at 77°K.

ment is broken down into carbon–hydrogen stretching, carbon–hydrogen bending, and the ring modes.

### Carbon–Hydrogen Stretching Vibrations

One characteristic of strained ring systems is the relatively high frequency of certain C–H stretching modes. In four-membered ring-molecules this mode has been assigned to the antisymmetric α-$CH_2$ stretching vibration.[11] In TMO, TMS, and TMSe the changing dipole moment of the mode lies at least approximately along the *C* axis. Therefore, the type-*C* contour of this high-frequency vibration is expected. The fact that the band (3008 $cm^{-1}$) has apparently shifted upon α-deuteration (2262 $cm^{-1}$) confirms that it arises from motion involving the α-hydrogen atoms. The corresponding Raman lines are not strongly polarized.

Of the four symmetric C–H stretching modes, two arise from the β-$CH_2$ group. In TMSe-$d_4$ two normal modes remain essentially unshifted at 2964 $cm^{-1}$ and 2936 $cm^{-1}$. The former appears to have a greater type-*C* contour than the latter and is assigned to the antisymmetric β-$CH_2$ stretching mode. As expected, the symmetric β-$CH_2$ stretching vibration is lower in frequency and has more type-*A* character. This assignment is supported by a preliminary normal coordinate calculation. A third moderately strong band at 2850 $cm^{-1}$ is undoubtedly an overtone of a deformation vibration enhanced in intensity by Fermi resonance.

In the carbon–deuterium stretching region there are four prominent Raman lines. At first it would seem logical to assign each of these lines to the four remaining C–D stretching vibrations. However, the intense line of lowest frequency (2142 $cm^{-1}$) is strongly polarized, a fact which is not consistent with the strong type-*B* band at 2154 $cm^{-1}$ in the vapor phase spectrum of TMSe-$d_4$. Thus, it seems evident that the Raman and infrared bands represent two separate, distinct vibrational modes, one $A'$ and the other $A''$, respectively.

The nontotally symmetric vibrations in TMSe-$d_4$ are easily located. The type-*B* bands at 2224 $cm^{-1}$ and 2154 $cm^{-1}$ are assigned to the antisymmetric and symmetric α-$CH_2$ stretching modes, respectively. For TMSe the corresponding bands are assigned at 2964 and 2869 $cm^{-1}$, respectively. The $A'$ antisymmetric α-$CD_2$ stretching mode probably contributes to either or both of the bands at 2185 $cm^{-1}$ and 2142 $cm^{-1}$ in the Raman spectra. The relatively high intensity of the latter (despite the enhancement due to the overlapping $A''$ mode) suggests this position for the fundamental. The 2185-$cm^{-1}$ band is therefore assigned to an overtone; however, it must be mentioned that the two are probably highly mixed by Fermi resonance.

### Carbon–Hydrogen Bending Vibrations

There are two $A'$ and one $A''$ $CH_2$ deformation vibrations in trimethylene selenide. The modes appear as a

TABLE I. Frequencies ($cm^{-1}$) of the fundamental vibrations in TMSe and TMSe-$d_4$.

| Vib. no. | ir (band type) | ir (solid) | Raman (liquid, pol.) |
|---|---|---|---|
| | A. PMSe | | |
| | Symmetry species $A'$ | | |
| $\nu_1$ | 3008 (*C*) | 2998 | 2997 (?) |
| $\nu_2$ | 2967 (*A*) | 2958 | 2947 (*p*) |
| $\nu_3$ | 2939 (*A–C*) | 2936 | 2918 (*p*?) |
| $\nu_4$ | 2908 (*A–C*) | 2908 | 2902 (*p*?) |
| $\nu_5$ | 1486 (*A*) | 1482 | 1475 (*p*) |
| $\nu_6$ | 1444 (?) | 1442 | 1437 (*p*?) |
| $\nu_7$ | 1197 (*A*) | 1190 | 1188 (*p*?) |
| $\nu_8$ | 1133 (*A*) | 1120 | 1127 (*p*?) |
| $\nu_9$ | 939 (*A*) | 936 | 937 (*p*) |
| $\nu_{10}$ | 902 (*A*) | 904 | 905 (*p*) |
| $\nu_{11}$ | 833 (*C*) | 828 | 824 (*p*) |
| $\nu_{12}$ | 645 (*C*) | 653 | 650 (*p*) |
| $\nu_{13}$ | 418 (*A*) | 414 | 416 (*p*) |
| $\nu_{14}$ | 159 (*C*) | ··· | ··· |
| | Symmetry species $A''$ | | |
| $\nu_{15}$ | 2963 (*B*) | 2945 | 2944 (?) |
| $\nu_{16}$ | 2869 (?) | 2850 | 2957 (?) |
| $\nu_{17}$ | 1457 (?) | 1460 | 1449 (*dp*?) |
| $\nu_{18}$ | 1291 (*B*) | 1285 | 1286 (*dp*?) |
| $\nu_{19}$ | 1228 (*B*) | 1223 | 1226 (*dp*?) |
| $\nu_{20}$ | 1172 (?) | 1165 | 1175 (?) |
| $\nu_{21}$ | 993 (?) | 993 | 986 (?) |
| $\nu_{22}$ | 980 (?) | 969 | 981 (*dp*) |
| $\nu_{23}$ | 792 (?) | 790 | 791 (*dp*?) |
| $\nu_{24}$ | 570 (?) | ? | 563 (*dp*) |
| | B. TMSe-$d_4$ | | |
| | Symmetry species $A'$ | | |
| $\nu_1$ | 2964 (*A*) | 2942 | 2929 (*p*) |
| $\nu_2$ | 2936 (*A*) | 2926 | 2902 (*p*) |
| $\nu_3$ | 2262 (*C*) | 2254 | 2257 (?) |
| $\nu_4$ | 2192 (*A–C*) | 2182 | 2185 (*p*) |
| $\nu_5$ | 1453 (*A*) | 1448 | 1446 (*p*) |
| $\nu_6$ | 1122 (*A*?) | 1114 | 1116 (*p*) |
| $\nu_7$ | 1060 (*A*) | 1054 | 1056 (*p*) |
| $\nu_8$ | 1002 (*A*) | 992 | 996 (*p*) |
| $\nu_9$ | 802 (*C*) | 798 | 801 (*p*) |
| $\nu_{10}$ | 743 (*C*) | 730 | 731 (*p*) |
| $\nu_{11}$ | 681 (*A*) | 680 | 683 (?) |
| $\nu_{12}$ | 574 (*A*?) | 579 | 581 (*p*) |
| $\nu_{13}$ | 405 (*A*) | 402 | 404 (*p*) |
| $\nu_{14}$ | 136? | ··· | ··· |
| | Symmetry species $A''$ | | |
| $\nu_{15}$ | 2224 (*B*) | 2208 | 2234 (?) |
| $\nu_{16}$ | 2154 (*B*) | 2144 | 2142 (*p*) |
| $\nu_{17}$ | 1281 (*B*) | 1276 | 1277 (*dp*) |
| $\nu_{18}$ | 1192 (*B*) | 1187 | 1192 (*dp*) |
| $\nu_{19}$ | 1091 (*B*) | 1081 | 1086 (?) |
| $\nu_{20}$ | 978 (*B*) | 970 | 978 (?) |
| $\nu_{21}$ | 843 (*B*) | 837 | 829 (?) |
| $\nu_{22}$ | 823 (*B*) | 813 | 810 (*dp*) |
| $\nu_{23}$ | 610 (?) | 614 | 630 (*dp*) |
| $\nu_{24}$ | ··· | 537? | 528 (?) |

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[11] W. G. Rothschild, J. Chem. Phys. **45**, 3599 (1966).

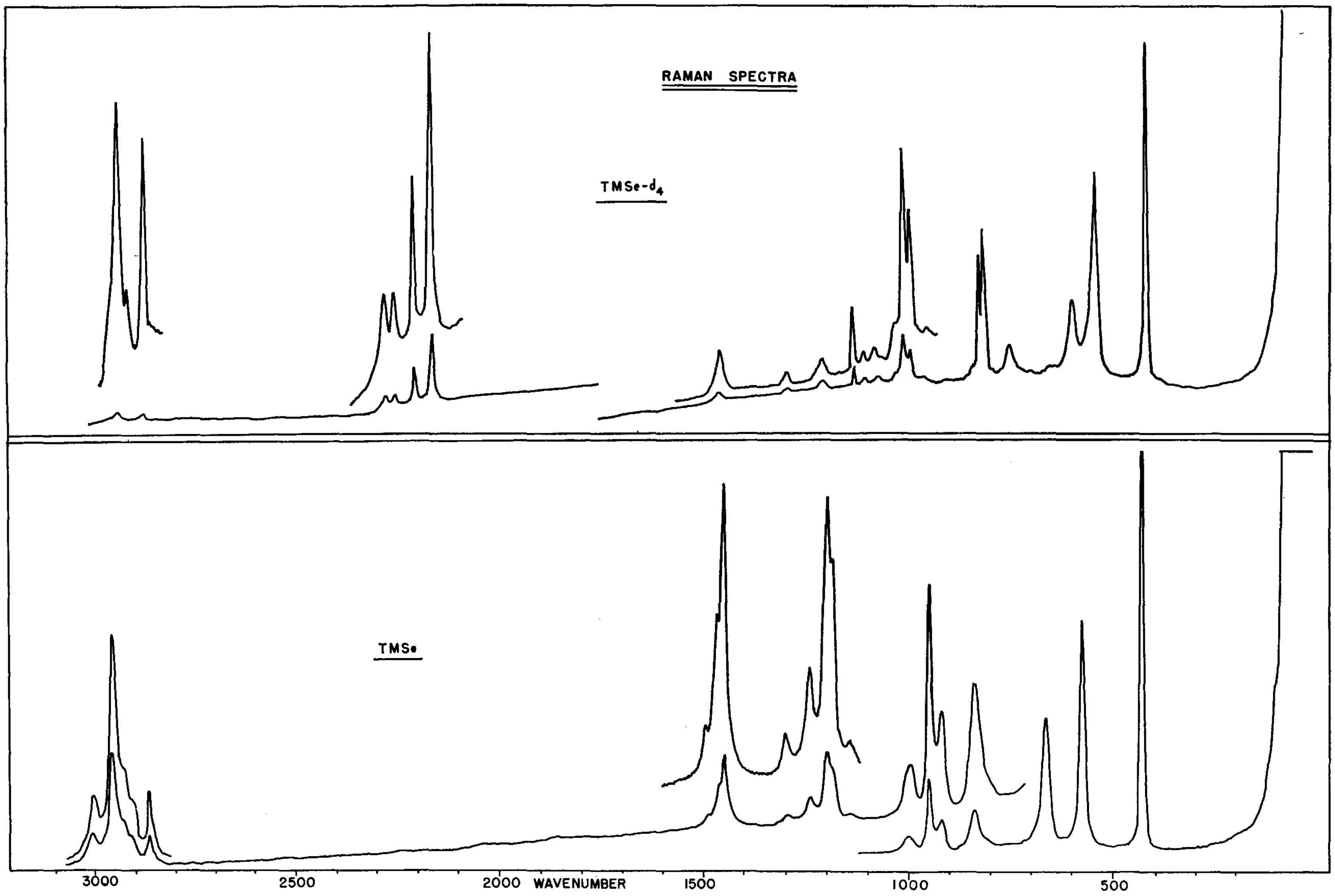

FIG. 3. The Raman spectra of liquid trimethylene selenide and trimethylene selenide-$d_4$.

triplet which is barely resolved in the Raman effect of the "light" compound near 1450 $cm^{-1}$. All three peaks have a relatively high depolarization ratio; the middle peak with the highest is assigned to the $A''$ vibration. The vapor-phase spectrum also reveals three absorption peaks which are assigned to these modes. The most intense (type $A$) band at 1444 $cm^{-1}$ is undoubtedly the $A'$ $\beta$-$CH_2$ deformation, since it remains essentially unshifted and of high intensity upon $\alpha$-deuteration. The other $A'$ mode, the $\alpha$-$CH_2$ deformation, appears as a weak type-$A$ band at 1486 $cm^{-1}$. The band at 1457 $cm^{-1}$ is expected to be the result of the $A''$ vibration. Unfortunately, the band contour is somewhat obscured since it lies on the shoulder of the $A'$ $\beta$-$CH_2$ deformation. However, a shift of about 7 $cm^{-1}$ upon condensation to the liquid state is very similar to the shift which appears for the two $A'$ modes.

The two $\alpha$-deformation vibrations in TMSe-$d_4$ are assigned to the type-$A$ and type-$B$ bands at 1192 $cm^{-1}$ ($A'$) and 1122 $cm^{-1}$ ($A''$), respectively. A preliminary normal coordinate calculation supports this assignment. Also, it should be mentioned that the analogous modes in TMO-$d_6$[12] are assigned at 1208 $cm^{-1}$ and 1116 $cm^{-1}$.

The type-$B$ band at 1291 $cm^{-1}$ in TMSe and slightly shifted in TMSe-$d_4$ is undoubtedly due to the $\beta$-$CH_2$ wagging vibration. It is expected to lie in this wavenumber region from information available on other molecules and is supported by the normal coordinate calculation. The two $\alpha$-wagging motions in TMSe are assigned to the type-$B$ band ($A''$) at 1228 $cm^{-1}$ and type-$A$ band ($A'$) at 1197 $cm^{-1}$. The bands are definitely shifted upon deuteration and become badly mixed with other symmetry coordinates in the heavy compound.

At this point the assignment becomes more difficult due to the increasing mixing of symmetry coordinates and other complicating circumstances. Moreover, the two nontotally symmetric $CH_2$ twisting modes are expected to be rather weak in the infrared, since they are inactive in the planar configuration. However, the very weak type-$B$ band at 1172 $cm^{-1}$, which is obscured by neighboring absorption, is a rather likely candidate for the $\beta$-twisting vibration ($A''$). The band is quite evident in the Raman effect and in the spectra of the deuterated species. The infrared activity of this band provides additional evidence for the nonplanarity of the ring skeleton. The other nontotally symmetric twisting mode, the $\alpha$-twisting motion, is assigned to the weak infrared band of uncertain contour near 993 $cm^{-1}$. In the Raman effect it appears as one component of an unresolved doublet. In TMSe-$d_4$ the vibration is probably highly mixed. The ($A'$) $\alpha$-twisting vibration is not expected to be a weak vibration in the infrared in contrast with the two $A''$ modes since it is not inactive in the planar molecule. The strong type-$A$ band (weak in the Raman) at 1133 $cm^{-1}$ is assigned to this mode. A band at 1136 $cm^{-1}$ has been assigned to the corresponding vibration in TMO.[12]

The rocking modes of trimethylene selenide are unfortunately highly mixed with several other symmetry vibrations. The $A''$ $\alpha$-rocking motion in TMSe is expected to be weak in the infrared, since it is inactive in the planar species. It is assigned, therefore, to the lower-frequency component of the weak doublet found in the Raman effect at 981 $cm^{-1}$. The band appears very weakly at 980 $cm^{-1}$ in the infrared of the vapor. The higher-frequency component has already been assigned to the $\alpha$-twisting vibration. Upon deuteration, the components of the doublet apparently shift to 843 and 827 $cm^{-1}$ and become considerably enhanced in intensity because of increased coupling with other symmetry modes.

The $A'$ $\alpha$- and $\beta$-rocking vibrations contribute considerably to the construction of several normal vibrations. However, our preliminary calculation seems to indicate major contributions to the bands at 902 and 833 $cm^{-1}$ in the spectrum of TMSe vapor. In the deuterated species the assignments are even more tenuous, but it appears that the type-$C$ band at 743 $cm^{-1}$ contains appreciable rocking motion.

## Ring Modes

As in the case for many of the methylene motions, the ring modes are usually strongly mixed with several symmetry vibrations. However, some simplification can result by classification of the four stretching vibrations as symmetric and antisymmetric C–Se and C–C stretching motions. The more highly mixed C–C vibrations are assigned to bands at 645 $cm^{-1}$ ($A'$) and 792 $cm^{-1}$ ($A''$). In TMSe-$d_4$ they apparently make major contributions at 610 $cm^{-1}$ ($A''$) and 574 $cm^{-1}$ ($A'$). The remaining ring stretching modes are easiest to assign. Since they involve C–Se stretching motion, these vibrations are expected to appear most strongly in the Raman spectrum. By far the strongest line is at 416 $cm^{-1}$ in TMSe and 404 $cm^{-1}$ in TMSe-$d_4$. Both lines are strongly polarized and appear as moderately strong type-$A$ bands in the infrared of the vapor. The normal coordinate calculations support the assignment of the bands as the symmetrical C–Se stretching vibration. It should be mentioned that the frequency of this mode is more than a hundred wavenumbers lower than in analogous acyclic molecules such as dimethyl diselenide[13] and methaneselenol,[14] both of which have (symmetrical) C–Se stretching vibrations at 584 $cm^{-1}$. Furthermore, it has been shown[10] that the band is no longer found at such low frequencies in polymerized TMSe. Therefore, the frequency shift is largely the result of the strained ring system.

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[12] W. J. Lafferty, Ph.D. thesis, Department of Chemistry, Massachusetts Institute of Technology, December 1960.

[13] W. H. Green and A. B. Harvey, J. Chem. Phys. **49**, 3586 (1968).

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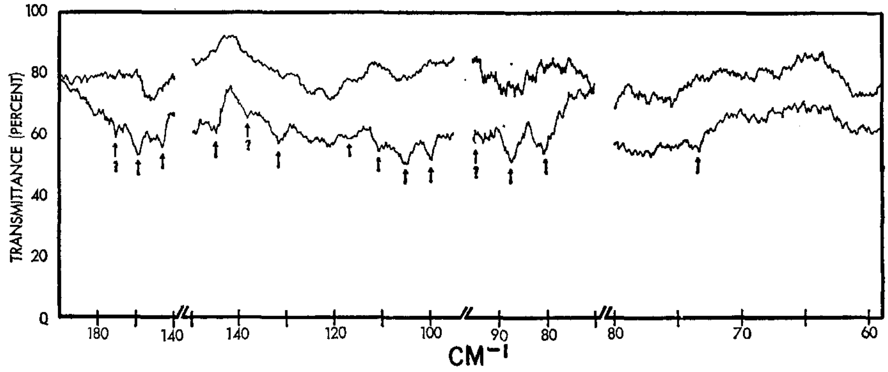

FIG. 4. The far-infrared spectrum of trimethylene selenide.

The antisymmetrical C–Se stretching vibration, on the other hand, appears as the second most intense line in the Raman effect at 563 and 528 $\text{cm}^{-1}$ in TMSe and TMSe-$d_4$, respectively. Both lines are depolarized. In contrast to the fairly strong symmetrical component, the antisymmetrical C–Se stretching vibration in either TMSe or TMSe-$d_4$ is very weak in the infrared. The position of the bands are also more indicative of the acyclic compounds.

In four-membered ring molecules there are two ring deformation vibrations. One of these approximates the in-plane bending motion of the planar species, but like many of the other modes in the "fingerprint region" of the infrared, this vibration is very highly mixed. Nevertheless, the motion probably contributes considerably to the intense infrared band at 939 $\text{cm}^{-1}$ in TMSe. The other ring mode is the ring-puckering vibration which will be described separately in some detail.

## FAR-INFRARED SPECTRA AND THE RING-PUCKERING VIBRATION

The far-infrared (double-beam) spectrum of trimethylene selenide in the vapor phase appears in Fig. 4. Not unlike trimethylene sulfide, it consists of a series of

TABLE II. Calculated and observed ring-puckering transitions ($\text{cm}^{-1}$) in trimethylene selenide.

| | | | Far-ir | | Mid-ir | |
|---|---|---|---|---|---|---|
| Trans | Calc freq | Calc rel int | ir-11 | *FS*-520 | Comb | Diff |
| 0–1 | 0.020 | $10^{-6}$ | ··· | ··· | ··· | ··· |
| 1–2 | 159.3 | (1.0) | 159 | 158.0 | 158.0 | ··· |
| 2–3 | 1.67 | $10^{-3}$ | ··· | (1.7) | ··· | ··· |
| 3–4 | 116.0 | 0.67 | 117 | ··· | 116.0 | 116.9 |
| 4–5 | 28.0 | 0.12 | ··· | ··· | 28.1 | 28.5 |
| 5–6 | 78.1 | 0.56 | 80 | ··· | 78.7 | 78.7 |
| 6–7 | 73.8 | 0.45 | 74 | ··· | 73.9 | 74.2 |
| 7–8 | 86.4 | 0.46 | 88 | 86.5 | 86.7 | 86.4 |
| 8–9 | 93.2 | 0.38 | 93 | 93.0 | 93.2 | 93.3 |
| 9–10 | 99.8 | 0.29 | 100 | 99.5 | 99.7 | 99.6 |
| 10–11 | 105.7 | 0.21 | 106 | 105.0 | 105.9 | 105.2 |
| 11–12 | 111.1 | 0.15 | 111 | 111.5 | 110.5 | 110.9 |
| 12–13 | 116.2 | 0.10 | 117 | 116.5 | 116.0 | 116.9 |
| 13–14 | 120.8 | 0.06 | ··· | 120.5 | 120.9 | 120.7? |
| 14–15 | 125.4 | 0.04 | 127? | 127? | 125.6 | 124.4? |
| 15–16 | 130.1 | 0.02 | 133? | 133?? | 129.5? | ··· |
| 16–17 | 134.5 | 0.01 | ··· | ··· | ··· | ··· |
| 0–3 | 161.0 | ··· | ··· | 160.2 | ··· | ··· |
| 2–5 | 145.7 | ··· | 145 | 146.2 | 146.0 | ··· |
| 4–7 | 179.9 | ··· | ··· | 179.5? | 180.0? | ··· |

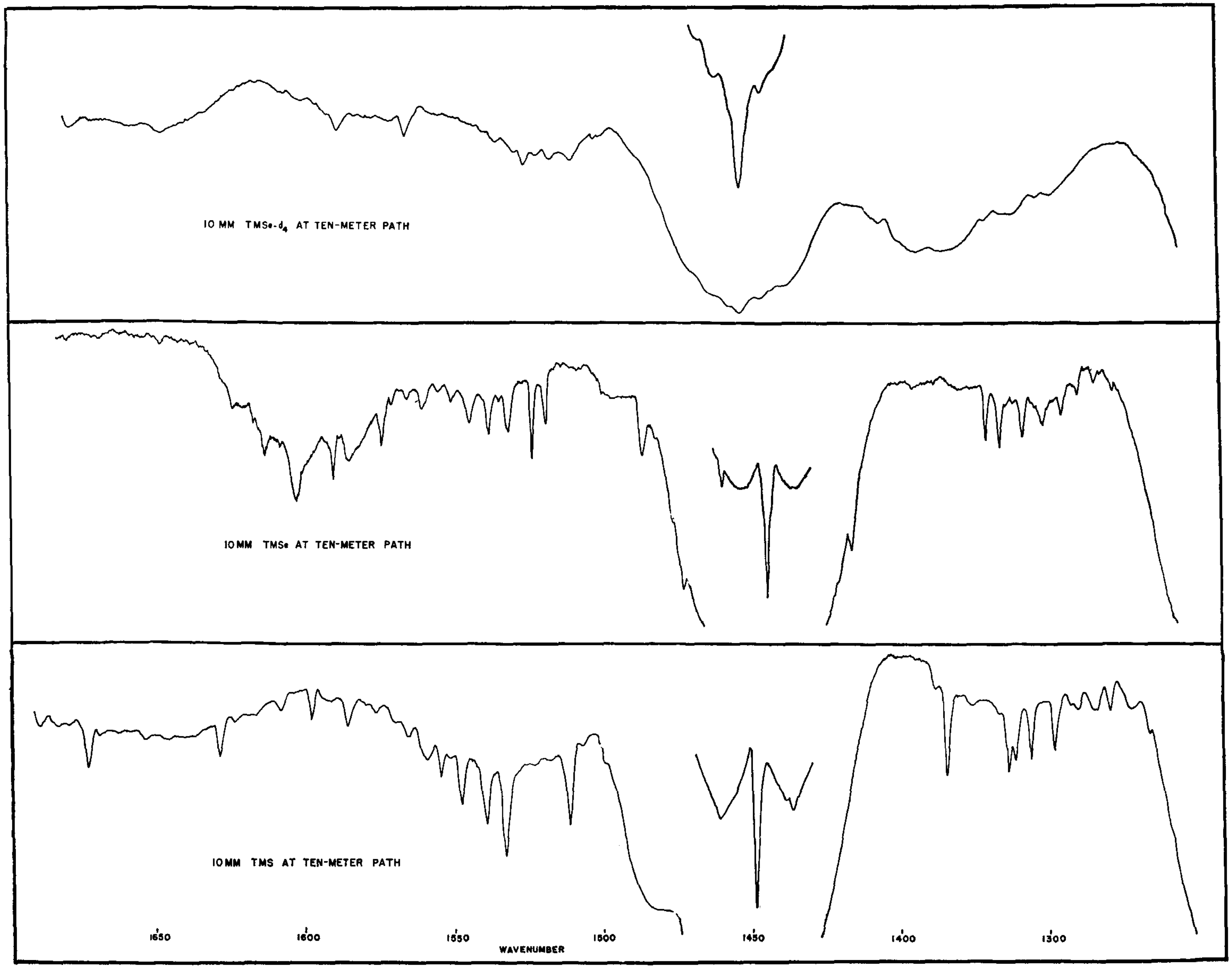

FIG. 5. Expanded-scale infrared spectra of trimethylene sulfide, trimethylene selenide, and trimethylene selenide-$d_4$ in the methylene deformation region.

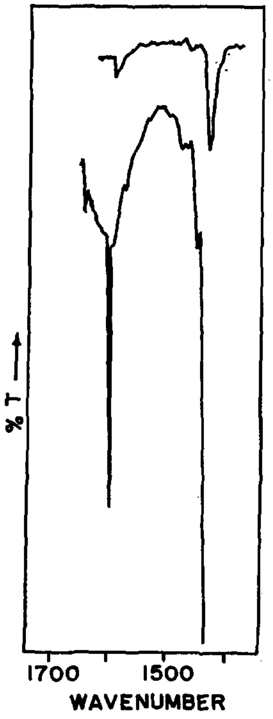

FIG. 6. Infrared spectrum in the methylene deformation region of trimethylene selenide in argon matrix at 20°K. The lower curve is the spectrum recorded at 10× ordinate expansion. The unit of the abscissa is cm$^{-1}$.

sharp $Q$ branches which are somewhat irregularly spaced. The frequencies of the $Q$ branches were checked on an interferometer and appear in Table II. It may be mentioned that the observation of irregular spacing of the $Q$ branches is strong evidence in itself for favoring a nonplanar structure.

Confirmation of the far-infrared bands was found in a previously reported[6] series of combination and difference bands of a methylene deformation vibration (near 1450 cm$^{-1}$) with the ring-puckering vibration. The expanded scale spectra of TMS, TMSe, and TMSe-$d_4$ in this region appear in Fig. 5. The remarkable agreement between the combination-difference data and the far-infrared frequencies in TMS and TMSe has already been demonstrated (see Table II and Ref. 6). However, it should be pointed out that in some cases the frequencies of ring-puckering transitions obtained from mid-infrared data have been found to deviate from those obtained from the far-infrared, as has been recently demonstrated.[15] Of course, with these considerations in mind and in cases where the far-infrared spectrum is weak or inactive, the combination-difference tones can be of considerable aid in understanding the molecular structure. For example, very recent experiments[16] have definitely established the barrier height in cyclobutane by the observation of such combination-difference series in the mid-infrared spectrum of the molecule whose elusive barrier height has been the topic of numerous discussions.

The assignment of the ring-puckering frequencies of TMSe appears in Table II and is based on the following arguments. As mentioned earlier, TMSe is expected to have at least two pairs of split levels below the top of the barrier. The 159-cm$^{-1}$ band, which is assigned to the transition(s) between the two lowest pairs of levels, is the most intense band in the far-infrared spectrum. Moreover, it is the only remaining band in the combination series near 1450 cm$^{-1}$ (see Fig. 6) in the spectrum of TMSe embedded in an argon matrix cooled by liquid hydrogen. At these temperatures nearly every molecule resides at the bottom pair of ring-puckering levels and the "hot" transitions vanish. It is interesting to note that in the combination series of bands in the vapor-phase spectrum of TMS and probably TMSe at room temperature, this transition is considerably weaker than those levels lying above the top of the barrier. This observation is not unreasonable if one considers that transitions which occur above the top of the barrier are much more anharmonic than those occurring within the double well. Since the intensities of combination bands are dependent on the magnitude of transition moments which are constructed from anharmonic terms in the potential, it is therefore not surprising that transitions below the top of the barrier are decidedly weaker than those just above the barrier. Of course, the Boltzmann factor inevitably dominates and weakens all of the transitions with increasing quantum number.

The band at 28 cm$^{-1}$ found in combination and difference is also an aid to the assignment. Since the third pair of levels is expected to be near the top of the barrier, the splitting of these levels is likely to be large but not larger than the transitions which occur above the barrier. The band at 28 cm$^{-1}$ obtained from the mid-infrared is a likely candidate for this transition and is confirmed by a calculation to be discussed later. A

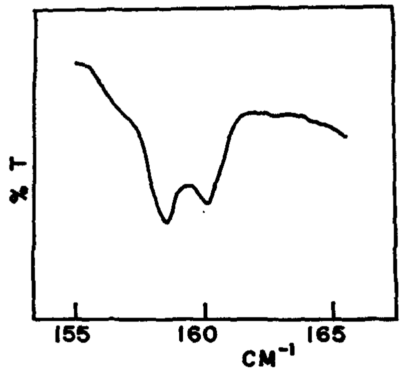

FIG. 7. Higher-resolution, far-infrared spectrum of trimethylene selenide, revealing the splitting of the $2\leftarrow1$ and $3\leftarrow0$ transitions.

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[15] W. H. Green and A. B. Harvey, J. Chem. Phys. **49**, 177 (1968).

[16] T. Ueda and T. Shimanouchi, J. Chem. Phys. **49**, 470 (1968). I. M. Mills (private communication).

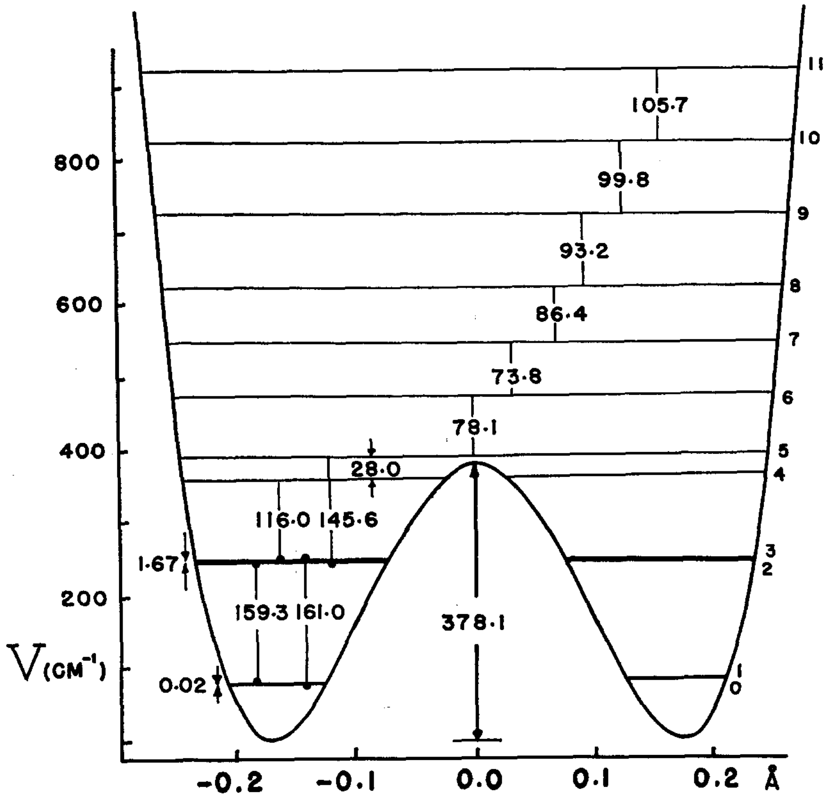

FIG. 8. The experimentally determined potential function, $V(\text{cm}^{-1}) = 4.258\times 10^5 x^4 - 2.5391\times 10^4 x^2$ ($x$ in angstroms), and its associated energy levels for the trimethylene selenide molecule.

search for the transition in the far infrared was not successful, presumably because of its low transition probability, low signal-to-noise ratio in this region of the spectrum, and the interference of overlapping pure rotational absorption.

Further confirmation of the assignment is found in the splitting of the second pair of levels, which has been estimated previously[6] to be about 1.7 cm$^{-1}$ and has been reproduced in a calculation to be discussed later. A higher-resolution interferometric spectrum (spectral slitwidth of 0.5 cm$^{-1}$) of the 159-cm$^{-1}$ band (see Fig. 7) reveals a splitting of about $1.5\pm0.3$ cm$^{-1}$, which agrees well with the predicted quantity.

In computing a potential function for the ring-puckering vibration in TMSe, we employed the observed frequencies, a trial potential function, and a computer program originally written by Ueda and Shimanouchi.[17] The form of the potential contained only a positive quartic and a negative quadratic term since this type of function has been so successful in the computations of levels of several ring molecules, including trimethylene oxide and sulfide. The opposite sign of the

TABLE III. Calculated energy levels for trimethylene selenide.

| Quantum no. | Energy (cm$^{-1}$) | Quantum no. | Energy (cm$^{-1}$) | Quantum no. | Energy (cm$^{-1}$) |
|---|---|---|---|---|---|
| 0 | 86.625 | 7 | 543.51 | 14 | 1276.60 |
| 1 | 86.645 | 8 | 629.89 | 15 | 1401.97 |
| 2 | 245.94 | 9 | 723.06 | 16 | 1532.06 |
| 3 | 247.62 | 10 | 822.86 | 17 | 1666.52 |
| 4 | 363.60 | 11 | 928.53 | 18 | 1803.80 |
| 5 | 391.59 | 12 | 1039.62 | 19 | 1954.49 |
| 6 | 469.72 | 13 | 1155.78 | 20 | 2111.59 |

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[17] T. Ueda and T. Shimanouchi, J. Chem. Phys. **47**, 4042 (1967).

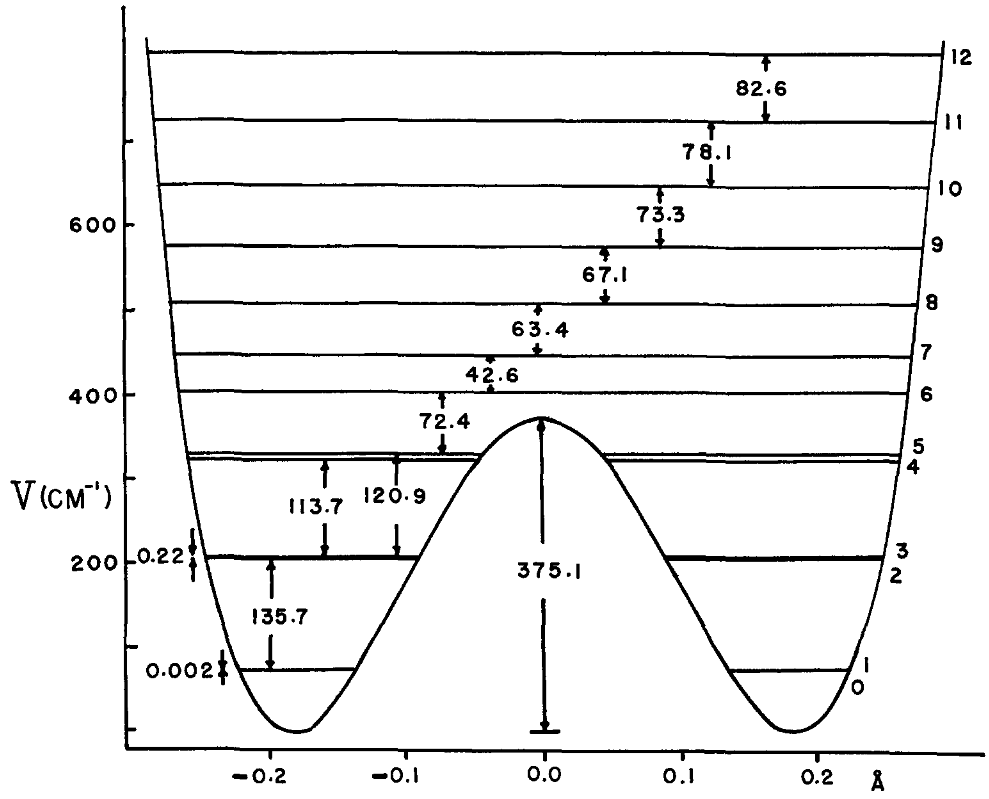

FIG. 9. The experimentally determined potential function, $V(\mathrm{cm}^{-1}) = 3.242\times10^5x^4 - 2.208\times10^4x^2$ ($x$ in angstroms), and its associated energy levels for the trimethylene selenide-$d_4$ molecule.

quadratic term creates the necessary hump for the nonplanar species. The Schrödinger equation was solved by constructing the Hamiltonian matrix from a basis set of 69 harmonic oscillator wavefunctions. The two coefficients of the trial potential function were then adjusted by an iterative procedure and the method of least squares until a best fit between calculated and observed frequencies was obtained.

In reduced form[5] the potential function can be written as

$$V(\mathrm{cm}^{-1}) = Z(z^4 - Bz^2),$$

where $z$ is the dimensionless, reduced coordinate for the ring-puckering mode. For TMSe the excellent agreement between observed and calculated frequencies, which is apparent in Table II, was obtained from the

TABLE IV. Calculated energy levels for trimethylene selenide-$d_4$.

| Quantum no. | Energy (cm$^{-1}$) | Quantum no. | Energy (cm$^{-1}$) | Quantum no. | Energy (cm$^{-1}$) |
|---|---|---|---|---|---|
| 0 | 71.521 | 7 | 443.41 | 14 | 985.00 |
| 1 | 71.523 | 8 | 506.85 | 15 | 1079.02 |
| 2 | 207.25 | 9 | 573.90 | 16 | 1176.41 |
| 3 | 207.47 | 10 | 647.19 | 17 | 1276.99 |
| 4 | 321.15 | 11 | 725.31 | 18 | 1380.61 |
| 5 | 328.34 | 12 | 807.88 | 19 | 1487.17 |
| 6 | 400.78 | 13 | 894.54 | 20 | 1596.54 |

following potential function:

$$V(\mathrm{cm}^{-1})=22.08(z^4-8.780z^2).$$

The height of the potential barrier in this function is 378.1±4 $\mathrm{cm}^{-1}$ (1.081±0.01 kcal/mole). If the reduced mass is known, the reduced function can be transformed into a nondimensionless coordinate. The reduced mass of TMSe has been calculated[18] to be 106.0 a.u., where the normal vibration is described as the separation of the ring diagonals, $2x$. In the usual way[5] the transformed potential function becomes

$$V(\mathrm{cm}^{-1})=4.258(\pm0.02)\times10^5x^4 -2.5391\pm0.007)\times10^4x^2,$$

where $x$ is in angstroms. A plot of this function appears in Fig. 8 and the energy of the ring-puckering levels in Table III. The minima in the potential occur at $x=0.173$ Å (the average value of $x=0.167$).

Trimethylene selenide-$d_4$ was synthesized to obtain confirmation of the assignment. Unfortunately, the far-infrared spectrum was so weak as to make any positive identification of peaks impossible. The $\alpha$-deuterated material was selected because the $\beta$-$\mathrm{CH_2}$ deformation was thought to be responsible for the strong fundamental giving rise to the satellite bands in the mid-infrared spectrum of TMSe. Figure 5 shows that the strong fundamental near 1450 $\mathrm{cm}^{-1}$ remains upon $\alpha$-deuteration, proving that a $\beta$-$\mathrm{CH_2}$ motion is responsible for the band. However, the deformation vibration in TMSe-$d_4$ is somewhat weaker and the central $Q$ branch is considerably more broadened than in TMSe. The resulting combination-difference bands are therefore broadened and weakened. Unfortunately, only a few satellite transitions are barely discernible in combination and the difference series is completely obscured by some moderate absorption of unknown origin. However, there are three bands which do appear consistently in every scan. These are observed at 136, 113, and 73 $\mathrm{cm}^{-1}$ and are tentatively assigned to the 2←1, 4←3, and 6←5 transitions, respectively.

The reduced mass of TMSe-$d_4$ has been estimated[18] to be 136.4 a.u. When this value of the reduced mass, the previous potential function, and the three observed frequencies are introduced into the computer program and the iteration procedure repeated, the following potential function is computed:

$$V(\mathrm{cm}^{-1})=3.242(\pm0.1)\times10^5x^4 -2.208(\pm0.033)\times10^4x^2,$$

where $x$ is in angstroms, or in reduced coordinates

$$V(\mathrm{cm}^{-1})=17.04(z^4-9.393z^2).$$

The potential function is plotted in Fig. 9 and the energies of the levels appear in Table IV. This potential represents a barrier of about 375 $\mathrm{cm}^{-1}$ which is in good agreement with the 378-$\mathrm{cm}^{-1}$ barrier found in the "light" compound. The minima occur at $x=0.18$ Å or $2x=0.36$ Å, which is to be compared with $2x=0.35$ Å for the light compound. From the diagonal separation, the dihedral angle[5] for both isotopic species is found to be 32.5±2° and does not deviate widely from this value for reasonable ring angles. This quantity compares favorably with the dihedral angle of 28° calculated for trimethylene sulfide[4] since a larger barrier in TMSe implies greater puckering and a larger dihedral angle.

In TMO and TMO-$d_6$ the reduced potential functions are $V(\mathrm{cm}^{-1})=28.2(z^4-1.47z^2)$ and $V(\mathrm{cm}^{-1})=21.9(z^4-1.68z^2)$, respectively.[5] Note that the corresponding coefficients in TMO and TMO-$d_6$ change in the same direction as in TMSe and TMSe-$d_4$. The small but significant differences in the two potential functions (in angstroms) is probably due to inadequate description of the normal coordinate as a simple, isolated motion of the ring (see Ref. 5). Finally, it should be mentioned that the calculation on TMSe-$d_4$ is based entirely on three very weak peaks in the mid-infrared which have not been confirmed in the far infrared. The results obtained from the assignment of these bands is, however, in good agreement with the information obtained from the "light" material.

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[18] D. O. Harris (private communication).