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Relativistic calculations of electronic states of TeH

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Relativistic configuration interaction calculations of five ω - ω states [$3/2$, $1/2$, $1/2(\text{II})$, $3/2(\text{II})$, $5/2$] of TeH are carried out. Comparison calculations of the $^2\Pi$ and $^4\Pi$ λ - s states are also carried out with the objective of understanding the effect of spin-orbit interaction on the electronic states of TeH. These calculations enable assignment of some of the experimentally observed spectra. The $1/2(\text{II})$, $3/2(\text{II})$, and $5/2$ states exhibit interesting avoided crossings.

I. INTRODUCTION

The electronic spectra of TeH and SeH have been the topics of a number of investigations.¹⁻⁶ A compilation of the experimental spectra of these molecules is found in the book by Huber and Herzberg.¹

The TeH molecule has not yet been investigated as much as SeH. Donovan *et al.*² have studied the vacuum UV spectra of SeH and TeH. While these authors observed a number of bands in the UV region, the resolution was insufficient to resolve the rotational structure. Thus, all the observed bands on TeH could not be assigned. The ESR investigation of Radford⁴ on TeH and SeH yielded the spin-orbit constant for the ground state of these molecules. Friedhoff *et al.*⁵ have recently investigated the negative ion photodetachment spectra of TeH^- . This study has revealed the electron affinities of group IV B hydrides.

Gibson *et al.*⁶ have recently carried out photoionization study of related species namely, SeH and H_2Se . This has yielded the ionization potential and dissociation energies of these molecules.

Theoretical investigation of the TeH molecule has not been undertaken up to now. The above survey of experimental works clearly demonstrates the need for such a calculation which would be valuable in the assignment of observed bands. The TeH molecule is also an interesting candidate for theoretical study since it has an open shell ground state ($^2\Pi$). Thus, spin-orbit splitting and contamination would be large for this system. We undertake this study with the objective of filling the abovementioned gaps. Theoretical studies of molecules containing very heavy atoms are being pursued vigorously.⁷⁻¹³ Section II outlines the method of our investigation while Sec. III contains results and discussions.

II. METHOD OF INVESTIGATION

Table I shows a few low-lying MO configurations of TeH, λ - s and ω - ω states arising from them. Since the outer shell of the Te atom is $5s^25p^4$, the bonding of the $5p$ orbital of Te with the hydrogen $1s$ orbital would lead to $1\sigma^22\sigma^21\pi^3$ configuration, where the 2σ orbital is the bonding MO re-

sulting from the interaction of Te ($5p_z$) with H ($1s$). The 1π orbital will essentially be nonbonding Te ($5p$). Thus, the spin-orbit splitting of the $^2\Pi$ state arising from the $1\sigma^22\sigma^21\pi^3$ configuration should be large. Table II shows the dissociation relationship of low-lying states of TeH.

In this investigation we carry out relativistic CI calculations of all the states dissociating into $^3P_2 + ^2S_{1/2}$ atoms. We employ relativistic effective core potentials for the Te atom which include spin-orbit interaction. Ermiler and Christiansen¹⁴ have recently reported analytical Gaussian fits of these potentials which we use in this study. We optimized a double-zeta Slater-type basis for the 3P ground state of the Te atom. The optimized exponents are shown in Table III. The hydrogen basis set is the same as the one employed in earlier PbH calculations.¹⁶ We include the $4d^{10}5s^25p^4$ outer shell of the Te atom in our SCF calculations. SCF calculations were carried out on the $^2\Pi$ electronic state of TeH to generate the orbitals for the CI calculations. The SCF calculations included the five d orbitals of Te and two σ and 1π orbitals arising from Te and H s and p orbitals as occupied orbitals. The d orbitals on Te were kept in core for the CI calculations. Relativistic configuration interaction calculations including spin-orbit interaction are carried out using the general method in Ref. 15. In this method, correlation and spin-orbit interaction are introduced simultaneously in a variational relativistic CI procedure.

In the relativistic CI procedure, in general, all ω - ω states of the same symmetry will mix with the amount of mixing determined by the spacing between the states. We include all low-lying λ - s configurations which give rise to an ω - ω state of the desired symmetry in the CI calculations. Table IV shows the number of reference configurations and the total number of configurations included in the CI calculations. The numbers reported in that table are for Cartesian configurations, since the relativistic CI code is set up for the C_{2v} point group. The $1/2$ states included $\sigma^2\pi^3$, $\sigma\sigma'\pi^3$, $\sigma\pi^4$, $\sigma'^2\pi^3$, $\sigma'\pi^4$, $\sigma^2\sigma'\pi^2$, and $\sigma\sigma'^2\pi^2$ configurations as reference configurations. The $3/2$ states included all of the above reference configurations except the $\sigma\pi^4$ and $\sigma'\pi^4$ reference configurations, since these do not yield a $3/2$ state. The $5/2$ state included six reference configurations arising from $^2\Delta_{5/2}$ and $^4\Pi_{5/2}$. Single and double excitations were allowed from these reference configurations. Thus, our CI calculations were MRSDCI (multireference singles plus doubles) CI calculation.

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TABLE I. λ -s and ω - ω states arising from low-lying MO configurations of TeH.

| MO configuration | λ -s state | ω - ω state |
|------------------------|--------------------|---------------------------|
| $\sigma^2\pi^3$ | $^2\Pi$ | 3/2, 1/2 |
| $\sigma\pi^4$ | $^2\Sigma^+$ | 1/2 |
| $\sigma\sigma'\pi^3$ | $^4\Pi$ | 5/2, 3/2, 1/2(2) |
| | $^2\Pi(2)$ | 3/2(2), 1/2(2) |
| $\sigma^2\sigma'\pi^2$ | $^4\Sigma^-$ | 3/2, 1/2 |
| | $^2\Sigma^-$ | 1/2 |
| | $^2\Sigma^+$ | 1/2 |
| | $^2\Delta$ | 5/2, 3/2 |

TABLE II. Dissociation limits for low-lying states of TeH.

| Molecular states | Dissociated atoms | Energy of the atoms* (cm ⁻¹) |
|--------------------|---------------------|--|
| 1/2, 1/2(II) 3/2 | $^3P_2 + ^2S_{1/2}$ | 0.0 |
| 3/2(II), 5/2 | | |
| 3/2(III), 1/2(III) | $^3P_1 + ^2S_{1/2}$ | 4751 |
| 1/2(IV) | | |

*From C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Stand. (U. S. GPO, Washington, D.C., 1971).

TABLE III. Optimized orbital exponents in Slater-type basis functions.

| | Te atom | H atom |
|---|-------------|-------------|
| s | 2.7825 (5s) | 1.1264 (1s) |
| | 1.5871 (5s) | 1.4108 (1s) |
| p | 2.5468 (5p) | 1.4409 (2p) |
| | 1.4904 (5p) | |
| d | 5.2079 (4d) | |
| | 3.0761 (4d) | |

TABLE IV. Numbers of reference and total configurations included in calculations for the low-lying states of each symmetry.

| State | Reference configuration | Total |
|---------|-------------------------|-------|
| 1/2 | 20 | 3746 |
| 1/2(II) | 22 | 4936 |
| 3/2 | 15 | 2584 |
| 3/2(II) | 16 | 3458 |
| 5/2 | 6 | 1992 |

III. RESULTS AND DISCUSSIONS

Figure 1 shows the calculated potential energy curves of 3/2, 1/2, 3/2(II), 1/2(II), 5/2, $^2\Pi$ and $^4\Pi$ states. The energies of the $^4\Pi$ and $^2\Pi$ states were obtained by omitting spin-orbit interaction. Table V shows the spectroscopic properties of the bound states among these. The calculated T_e of the 1/2 state (3989 cm⁻¹) is in reasonable agreement with the somewhat uncertain value of 3830 cm⁻¹ obtained from

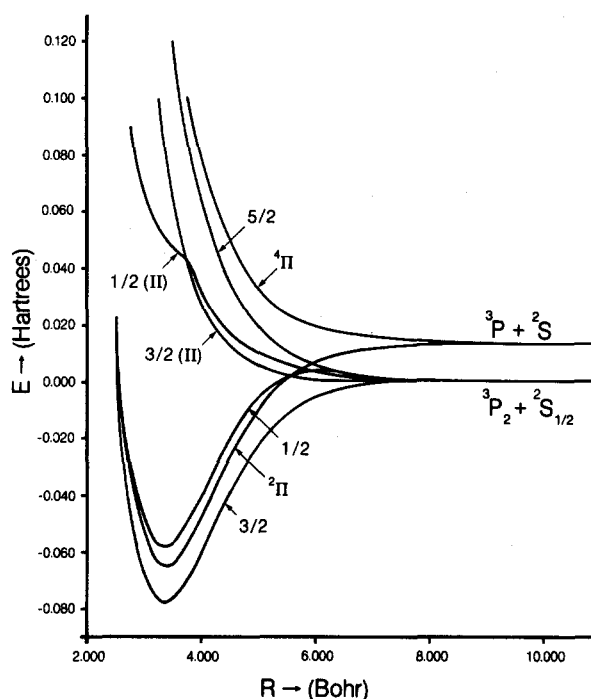


FIG. 1. Potential energy curves of low-lying states of TeH.

the interpretation of the VUV absorption spectrum of TeH.² Our equilibrium bond length of TeH (1.767 Å) is also in very good agreement with an uncertain experimental value of 1.74 Å as quoted by Huber and Herzberg.¹ The X_2-X_1 transition has not yet been observed directly. There are no experimental ω_e values for the 3/2 and 1/2 states.

Thus, the theoretical values reported in Table V should be useful for future experimental vibrational and rotational analysis. The calculated dissociation energy of the X_1 (3/2) ground state is 2.31 eV. This value is about 0.04 eV lower than the corresponding $^2\Pi$ λ -s state. The D_e value of the 1/2 state is, however, much lower (1.8 eV), which is due to the significant spin-orbit splitting and contamination of this state. Since our calculated D_e values are about 75% to 85% of the experimental values due to neglect of higher-order electron correlations, it is predicted that the D_e value of the ground state should be about 2.75–3.00 eV.

As one can see from Fig. 1, the 1/2(II), 3/2(II), and 5/2 curves are repulsive. Thus, transitions from the two spin-orbit components (X_1 , X_2) of the ground state to these states can be seen only in absorption. This is consistent with the known experimental spectra of TeH. There are four ab-

TABLE V. Spectroscopic properties of low-lying states of TeH.

| State | T_e (cm ⁻¹) | R_e (Å) | ω_e (cm ⁻¹) | D_e (eV) |
|---------|---------------------------|-----------|--------------------------------|------------|
| 3/2 | 0.0 | 1.767 | 1839 | 2.31 |
| 1/2 | 3989 | 1.764 | 1845 | 1.81 |
| $^2\Pi$ | 2449 | 1.763 | 1855 | 2.35 |

TABLE VI. Contributions of various configurations to the electronic states of TeH. Numbers in parentheses are percentages.

| State | R (bohr) | Contributions |
|---------|----------|--|
| 3/2 | 3.50 | $1\sigma^2 2\sigma^2 1\pi^3$ (95), $1\sigma^2 3\sigma^2 1\pi^3$ (2) |
| 3/2 | 5.00 | $1\sigma^2 2\sigma^2 1\pi^3$ (77), $1\sigma^2 3\sigma^2 1\pi^3$ (13), $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ ($^4\Sigma^-$; 3), $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ ($^2\Delta$; 1) |
| 3/2 | 7.00 | $1\sigma^2 2\sigma^2 1\pi^3$ (42), $1\sigma^2 3\sigma^2 1\pi^3$ (27), $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ (23), $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ ($^4\Sigma^-$; 1.4), $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ ($^2\Delta$; 2) |
| 1/2 | 3.50 | $1\sigma^2 2\sigma^2 1\pi^3$ (95), $1\sigma^2 3\sigma^2 1\pi^3$ (2) |
| 1/2 | 5.00 | $1\sigma^2 2\sigma^2 1\pi^3$ (70), $1\sigma^2 3\sigma^2 1\pi^3$ (12), $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ (7), $1\sigma^2 2\sigma 1\pi^4$ (2), $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ ($^4\Sigma^-$; 4) |
| 1/2 | 7.00 | $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ (54), $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ ($^4\Sigma^-$; 19), $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ ($^4\Sigma^-$; 16), $1\sigma^2 2\sigma^2 1\pi^3$ (5), $1\sigma^2 3\sigma^2 1\pi^3$ (4) |
| 1/2(II) | 3.50 | $1\sigma^2 2\sigma 1\pi^4$ (88), $1\sigma^2 3\sigma 1\pi^4$ (4) |
| | 3.75 | $1\sigma^2 2\sigma 1\pi^4$ (62), $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ (19), $1\sigma^2 3\sigma 1\pi^4$ (5), $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ ($^2\Sigma^+$; 3), $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ (3) |
| 1/2(II) | 4.00 | $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ (70), $1\sigma^2 2\sigma 1\pi^4$ (9), $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ (7), $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ (4), $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ ($^2\Sigma^+$; 4) |
| 1/2(II) | 5.00 | $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ (51), $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ (23), $1\sigma^2 2\sigma^2 1\pi^3$ (4), $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ ($^2\Sigma^+$; 2) |
| 3/2(II) | 3.00 | $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ ($^4\Sigma^-$; 94), $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ ($^4\Sigma^-$; 1.5) |
| 3/2(II) | 5.00 | $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ ($^4\Sigma^-$; 55), $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ ($^4\Sigma^-$; 16), $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ (22), $1\sigma^2 2\sigma^2 1\pi^3$ (4) |
| 3/2(II) | 6.00 | $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ (48), $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ ($^4\Sigma^-$; 20), $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ ($^4\Sigma^-$; 11.5), $1\sigma^2 2\sigma^2 1\pi^3$ (11), $1\sigma^2 3\sigma^2 1\pi^3$ (4) |
| 5/2 | 3.00 | $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ ($^2\Delta$; 74), $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ ($^4\Pi$; 20) |
| 5/2 | 3.50 | $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ ($^4\Pi$; 56), $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ ($^2\Delta$; 38) |
| 5/2 | 5.00 | $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ ($^4\Pi$; 92), $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ ($^2\Delta$; 2) |

sorption bands below $55\,000\text{ cm}^{-1}$ which are labeled $B \leftarrow X_1$, $C \leftarrow X_1$, $C \leftarrow X_2$, and $D \leftarrow X_1$. We calculated vertical separation of the 3/2(II), 1/2(II), and 5/2 states at 3.25 bohr [near r min of 3/2 (X_1)]. These splittings are 28 568, 39 000, and $52\,010\text{ cm}^{-1}$, respectively. The 1/2(II)–1/2 splitting at this distance is $24\,563\text{ cm}^{-1}$. Based on this splitting, the $B \leftarrow X_1$ transition could be tentatively assigned to 3/2(II) \leftarrow 3/2 transition. In any event, our calculations predict 1/2(II) \leftarrow 1/2(X_2), 3/2(II) \leftarrow 3/2(X_1), 1/2(II) \leftarrow X_1 (3/2), and 5/2 \leftarrow X_1 (3/2) transitions in the neighborhood of 25 000, 29 000, 39 000, and $52\,000\text{ cm}^{-1}$. Further analyses of the $B \leftarrow X_1$, $C \leftarrow X_1$, $C \leftarrow X_2$, and $D \leftarrow X_1$ bands are needed for unambiguous assignment.

Table VI shows the contributions of various configurations to the low-lying electronic states of TeH. As one can see from that table, the X_1 (3/2) ground state is dominantly $^2\Pi$ ($1\sigma^2 2\sigma^2 1\pi^3$) at near equilibrium r values. At larger internu-

clear separations ($R = 7.00$ bohr), mixing with other configurations such as $1\sigma^2 2\sigma^2 3\sigma 1\pi^3$, $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$ ($^4\Sigma^-$), etc. increase. X_2 (1/2) state is predominantly $^2\Pi_{1/2}$ at short r values. Spin-orbit mixing with other λ - s states such as $^4\Sigma_{1/2}^-$ become significant at larger internuclear distances (see Table VI).

The 1/2(II) and 5/2 states exhibit interesting avoided crossings. At short distances the 1/2(II) state is predominantly $^2\Sigma^+$ ($1\sigma^2 2\sigma 1\pi^4$). At about 4.00 bohr, this state becomes dominantly $^4\Sigma^-$ ($1\sigma^2 2\sigma^2 3\sigma 1\pi^2$) although other states such as $^2\Sigma^-$, $^2\Sigma^+$, etc. also make appreciable contributions (see Table VI). This leads to the shoulder in the 1/2(II) curve (see Fig. 1). The 5/2 state is predominantly $^2\Delta_{5/2}$ at short distances but is mainly $^4\Pi_{5/2}$ at intermediate and long distances. This avoided crossing, however, does not lead to a sudden change in the shape of the 5/2 curve.

The 3/2(II) state is predominantly $^4\Sigma_{3/2}^-$ at short distances. At long distances, however, the $^4\Pi$ and $^2\Pi$ states arising from $1\sigma^2 2\sigma^2 3\sigma 1\pi^3$ configuration dominate. Thus, the 3/2(II) state also exhibits avoided crossings.

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