

Electron energy loss spectroscopy (EELS) of H₂O, H₂S, H₂Se and H₂Te*

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Abstract—Electronic excitation in H₂O, H₂S, H₂Se and H₂Te molecules has been studied by the EELS technique. Spectra of H₂S and H₂Se are remarkably similar with the 1b₁-nd transition most intense. The intensity of the first transition 1b₁-nsa₁ decreases through H₂O to H₂Se and this transition is absent in H₂Te. Transitions observed by EELS have been compared with optical absorption studies. A correlation diagram of the occupied and the excited states has been provided for these four molecules by making use of UVPES and EELS.

INTRODUCTION

Electron states of H₂O, H₂S, H₂Se and H₂Te have been reported by POTS and PRICE [1] employing u.v. photoelectron spectroscopy (UVPES). Several optical absorption studies in the vacuum u.v. region have been reported earlier [2-10]. All the electronic transitions in these molecules occur in the vacuum u.v. region and therefore electron energy loss spectroscopy (EELS) can provide a convenient method to study electronic excitation. Thus, electron impact spectra of H₂O has been reported by TAM and BRION [11]; ABUAIN *et al.* [12] have recently reported impact spectra of the H₂S molecule using an electron trap spectrometer near threshold. Hitherto, to our knowledge, energy loss spectra of H₂Se and H₂Te have not been reported in the literature. Further, a combined use of UVPES for the electron states of occupied orbitals with electronic excitation by EELS can provide energy level schemes of both occupied and excited states. Recently, we have studied I₂-diethyl ether [13] and BF₃-H₂O [14] complexes making use of UVPES and EELS. In an attempt to understand the electronic excitation in the near and far u.v. region, we considered it worthwhile to study EELS of the series of molecules H₂O, H₂S, H₂Se and H₂Te, all with C_{2v} symmetry. New excitation bands above 10 eV have been observed here which were not seen in the optical studies. We provide, for the first time, a correlation diagram of electron states in these related molecules by the combined use of UVPES and EELS techniques.

EXPERIMENTAL

Electron energy loss spectra of these molecules have been recorded in the home built spectrometer [15]. The primary electron beam energy was 40 eV with FWHM 280 meV. The spectra were taken at 0° scattering angle. H₂S was prepared by the standard method from Na₂S and H₂SO₄. H₂Se and H₂Te were prepared by reacting Al₂Se₃ and Al₂Te₃ with

HCl. The gases were dried over P₂O₅ and the u.v. photoelectron spectra were also taken to test the purity in the home built spectrometer [16]. The UVPES spectra of all the four molecules were exactly similar to those reported by POTS and PRICE [1].

RESULTS AND DISCUSSION

Electron energy loss spectra of H₂O, H₂S and H₂Se are given in Fig. 1. In Fig. 2 the loss spectra of H₂Te is shown. The excitation energies, term values, quantum defects and the transitions are summarized in Table 1.

UVPES of these molecules give three bands [1]. For example, in H₂O the highest occupied orbital, 1b₁, is the O(2p) lone pair orbital perpendicular to the molecular plane; the second band, 3a₁, is also due to an O(2p) lone pair, parallel to the plane, but it is partially mixed with the bonding 1b₂ orbital. The second orbital, 3a₁, tends more towards a lone pair like orbital as one goes from H₂O to H₂Te as is clear from the photoelectron peak becoming narrower [1]. The third band 1b₂, is the bonding orbital showing vibrational structure. We have taken a uniform notation for these three orbitals as 1b₁, 3a₁ and 1b₂ as in H₂O for the other three molecules. That is, highest occupied orbital in H₂Te, eg, is 1b₁ due to n_{Tc}, the second orbital is 3a₁ due to n̄_{Tc} and the third orbital 1b₂ due to σ_{Tc-H}.

The energy of the Rydberg states formed by excitation of a single electron to a Rydberg orbital can be well approximated by the formula: $E_n = A - [R/(n - \delta)^2]$, where E_n is the excitation energy, A is the ionization potential and δ is the quantum defect. We have used this for finding the δ values as has been done by TAM and BRION [11].

Energy loss spectra and the assignments in the case of H₂O are the same as that reported by TAM and BRION [11]. The excitation energies match within 0.1 eV. Some of the higher transitions reported by them are not seen here possibly because of slightly lesser resolution.

In H₂S, the first three excitation bands at 6.30, 8.27 and 8.90 eV all originate from the highest occupied 1b₁ like orbital and are excited to 4sa₁, 4pa₁ and 3d Rydberg states respectively. These transitions and the

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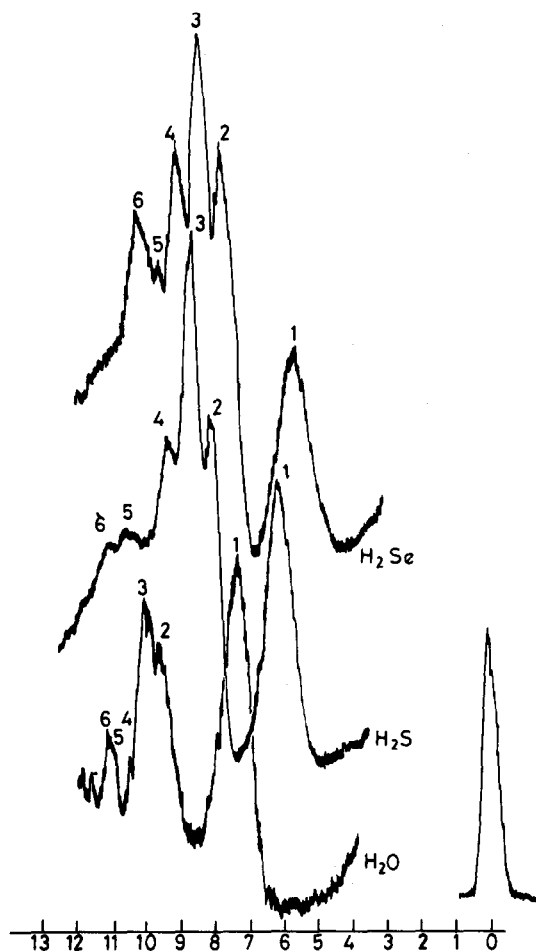


Fig. 1. Electron energy loss spectra of H_2O , H_2S and H_2Se .

assignments agree well with the optical absorption data [2-5, 10]. The values of quantum defect lend further support to these assignments (Table 1). The fourth band at 9.61 has been assigned to $3a_1-4s_{a_1}$ from the simple consideration of quantum defect with a value of 1.08. The 10.77 eV band is due to the ionization from $1b_1$. The band at 11.27 eV, not seen in optical studies, can be assigned to $3a_1-4p_{a_1}$.

Electronic excitation spectra of H_2S employing an electron trap spectrometer near threshold by ABUIAN *et al.* [12] show bands only up to 9.5 eV. Further, the relative intensities of bands differ considerably when the electron beam energy is around 40 eV. Thus, near threshold energies, $1b_1-4p$ is the most intense band [12] whereas the $1b_1-3d$ is the most intense band with the 40 eV beam as seen in our study. ABUIAN *et al.* find that the intensity is proportional to the excitation cross-section for electron energy in excess of the excitation threshold. Increasing this residual energy from 0.2 eV to 1 eV above the excitation energy, the relative intensity of $1b_1-3d$ increases with reference to $1b_1-4p$. The electron beam used in this experiment is about 3.5 times the excitation energy and at such primary beam energies, the optically allowed $1b_1-3d$ transition has the highest cross-section. This explains why $1b_1-3d$ ($1b_1$ is mainly of np in character) is more intense compared to $1b_1-4p$ transition.

There is complete band to band correspondence between the spectra of H_2S and H_2Se (Fig. 1). The relative intensities are also similar except that the intensity of the first band $1b_1-5s_{a_1}$ in H_2Se is lower compared to the $1b_1-4s_{a_1}$ band in H_2S , taken with reference to the most intense $1b_1-nd$ transition. In the case of H_2Se , the first band at 5.67 eV, assigned to $1b_1-5s_{a_1}$, has not been clearly observed in optical

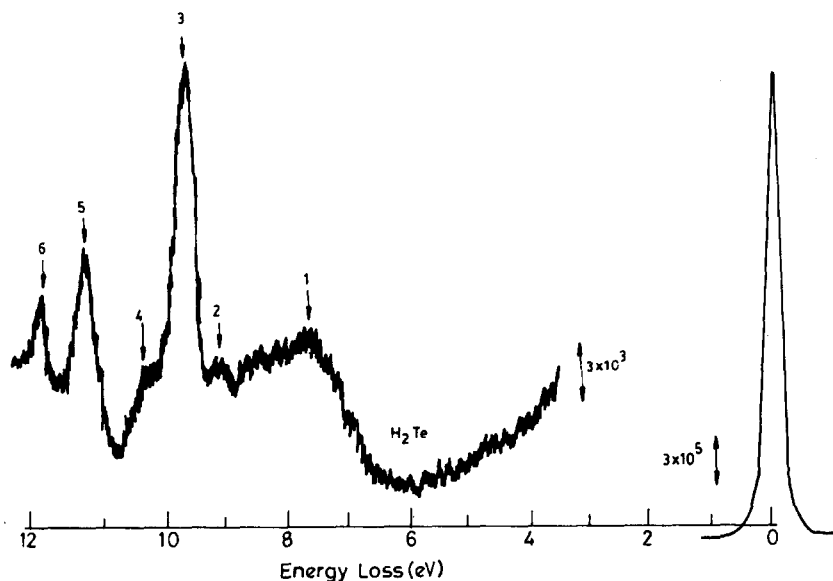


Fig. 2. Electron energy loss spectrum of H_2Te .

Table 1.

| Molecule | Excitation energy, E_n | Term value | Quantum defect δ | Assignment |
|-------------------|--------------------------|------------|-------------------------|----------------|
| H ₂ O | 7.31 | 5.31 | 1.34 | $1b_1-3sa_1$ |
| | 9.64 | 5.1 | 1.36 | $3a_1-3sa_1$ |
| | 10.00 | 2.62 | 0.72 | $1b_1-3pa_1$ |
| | 10.58 | 2.04 | 0.41 | $1b_1-3pb_1$ |
| | 11.04 | 1.58 | 1.06 | $1b_1-4sa_1$ |
| H ₂ S | 11.20 | 1.42 | 0.09 | $1b_1-3d$ |
| | 6.30 | 4.17 | 1.19 | $1b_1-4sa_1$ |
| | 8.27 | 2.20 | 0.51 | $1b_1-4pa_1$ |
| | 8.90 | 1.57 | 0.05 | $1b_1-3d$ |
| | 9.61 | 3.72 | 1.08 | $3a_1-4sa_1$ |
| H ₂ Se | 10.77 | 0 | — | $1b_1-H_2S^+$ |
| | 11.27 | 2.06 | 0.43 | $3a_1-4pa_1$ |
| | 5.67 | 4.21 | 1.20 | $1b_1-5sa_1$ |
| | 7.72 | 2.16 | 0.49 | $1b_1-5p$ |
| | 8.27 | 1.61 | 0.09 | $1b_1-4d$ |
| H ₂ Te | 8.98 | 3.95 | 1.14 | $3a_1-5sa_1$ |
| | 9.79 | 3.95 | 1.14 | $1b_1-H_2Se^+$ |
| | 10.17 | 2.76 | 0.78 | $3a_1-5p$ |
| | 7.59 | 1.55 | 0.03 | $1b_1-5d$ |
| | 9.06 | 0 | — | $1b_1-H_2Te^+$ |
| | 9.62 | 2.38 | 0.66 | $3a_1-6p$ |
| | 10.23 | 1.77 | 0.22 | $3a_1-5d$ |
| | 11.21 | 2.04 | 0.41 | $1b_2-6p$ |
| | 11.94 | 1.31 | -0.22 | $1b_2-5d$ |

studies [2–5]. The second and third bands at 7.72 and 8.27 eV match well with the optical studies to within 0.1 V and the transitions reported here are in accordance with optical studies. The fourth band at 8.98 eV observed here has been assigned to $3a_1-5sa_1$ and it is similar to the corresponding band in H₂S at 9.61 eV. The excitation band at 9.79 eV in H₂Se coincides with the first ionization energy of H₂Se at 9.88 eV. The last

and the distinct band at 10.17 eV above the ionization limit has been assigned to $3a_1-5p$.

H₂Te shows an entirely different electron loss spectrum compared to H₂O, H₂S and H₂Se. The first band is found at around 7.59 eV. This is assigned to a $1b_1-5d$ transition with the quantum defect value of 0.03 and agrees with the optical studies [2–4]. The weak second band at 9.06 eV coincides with the first ionization

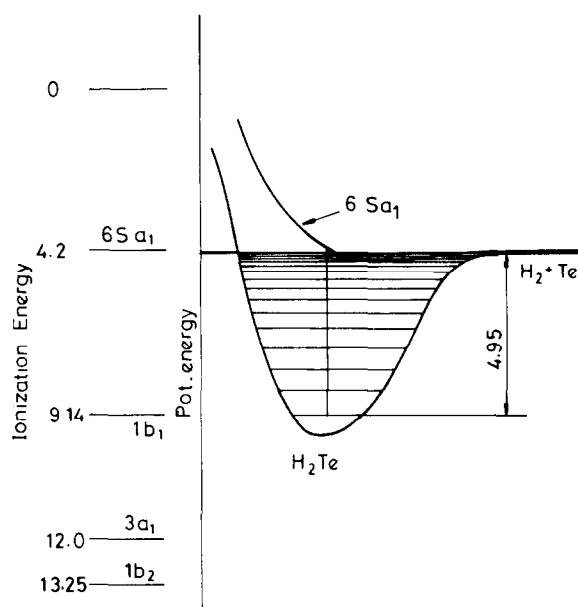


Fig. 3. Schematic diagram showing $6sa_1$ level in H₂Te lying in the dissociation continuum. Electronic transition to this state leads to dissociation.

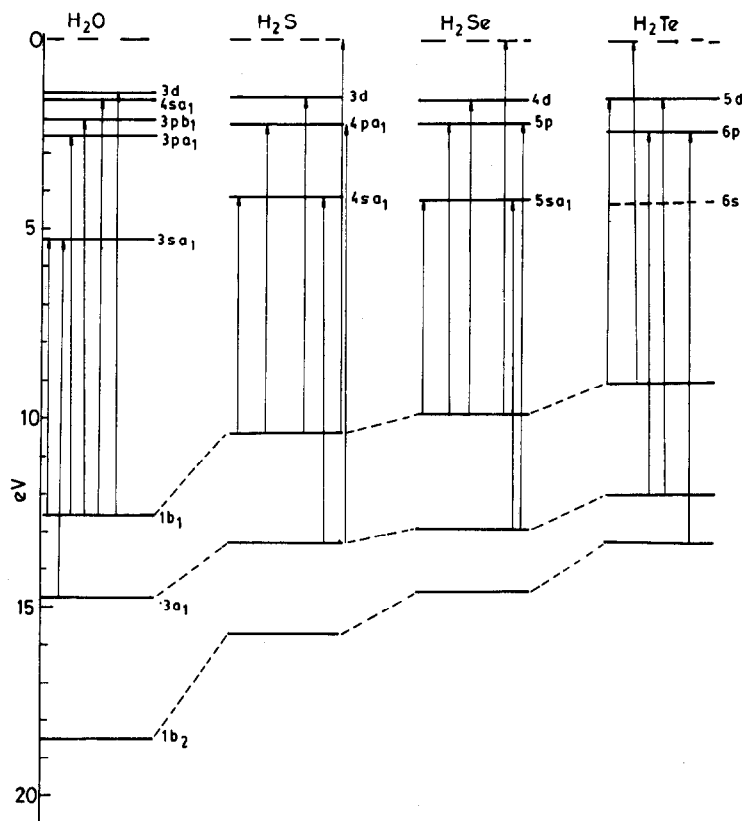


Fig. 4. Correlation diagram of electronic states in H_2O , H_2S , H_2Se and H_2Te and the electronic transitions.

band of H_2Te at 9.14 eV. The next four bands at 9.62, 10.23, 11, 21 and 11, 94 eV above the first ionization limit seem to originate from the $3a_1$ and $1b_2$ orbitals. The assignments are given in Table 1.

Unlike H_2O , H_2S and H_2Se , we do not see any band due to a $1b_1-6sa_1$ transition in H_2Te . The intensity of the first band, $1b_1-nsa_1$ ($n=3, 4, 5$ for O, S and Se respectively), in H_2O , H_2S and H_2Se successively decreases. Correspondingly, in H_2O , the quantum defect for the $3sa_1$ is rather high (1.34) indicating that it is more like a molecular orbital than a Rydberg state. However, the value decreases to 1.2 in H_2S and H_2Se implying this to be more like a Rydberg state. It is also important to note the excitation from $3a_1-6sa_1$ as well as $1b_2-6sa_1$ are not observed. Optical excitation from $1b_1-6sa_1$ has not been observed. Bond dissociation energy of $\text{H}_2\text{Te} \rightarrow \text{H}_2 + \text{Te}$ is 4.9 eV [17]. In comparison with H_2O , H_2S , H_2Se , the first excitation should occur around 5 eV thus giving the term value of 4.17 eV for $6sa_1$, by taking the value of ionization energy of $1b_1$ in H_2Te equal to 9.14 eV [1]. Dissociation energy of H_2Te being 4.94 eV, the $6sa_1$ can lie in the dissociation continuum preventing the $6sa_1$ being a good stationary state. This is shown schematically in Fig. 3. Thus, excitation from any of the occupied levels to $6sa_1$ leads to dissociation and hence the transitions are not observed. This could be the reason why the optical transition is also not observed.

Based on the assignments discussed above a correlation diagram of the occupied as well as the Rydberg states has been given in Fig. 4. The vertical ionization energies for the $1b_1$, $3a_1$ and $1b_2$ states have been taken from the UVPES studies [1]. The likely position of $6sa_1$ in H_2Te is indicated by a dashed line. Major transitions as observed by EELS can thus be described by this scheme.

CONCLUSIONS

Electronic excitation from the electron energy loss spectra of H_2O , H_2S , H_2Se and H_2Te have been assigned from simple considerations of quantum defect and they do agree well with optical absorption studies. Intensity of the first band, $1b_1-nsa_1$ decreases with the series H_2O to H_2Se , and this band is absent in H_2Te . A correlation diagram of the electron states for these molecules has been provided by the combined use of UVPES and EELS.

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REFERENCES

- [1] A. W. POTS and W. C. PRICE, *Proc. R. Soc., Lond.* **A326**, 181 (1972).
- [2] W. C. PRICE, J. P. TEEGAN and WALSCH, *Proc. R. Soc., Lond.* **A201**, 600 (1950).
- [3] J. P. CONNERADE, M. A. BAIG, S. P. MCGLYN and W. R. S. GARTON, *J. Phys. B, atom. molec. Phys.* **13**, L705 (1980).
- [4] J. M. HOLLAS and Z. R. LEMANCZYK, *J. molec. Spectrosc.* **66**, 79 (1977).
- [5] P. HELMINGER and F. C. DELUCIA, *J. molec. Spectrosc.* **8**, 300 (1962).
- [6] K. J. MILLER, S. R. MIELCZAREK and M. KRAUSS, *J. chem. Phys.* **51**, 26 (1969).
- [7] C. A. MAYHEW, M. A. BAIG and J. P. CONNERADE, *J. Phys.* **B16**, L757 (1985).
- [8] C. A. MAYHEW and J. P. CONNERADE, *J. Phys.* **B19**, 3505 (1986).
- [9] C. A. MAYHEW and J. P. CONNERADE, *J. Phys.* **B19**, 3493 (1986).
- [10] H. MASUKA, Y. MORIHA and M. NAKAMURA, *Can. J. Phys.* **57**, 745 (1975).
- [11] W. C. TAM and C. E. BRION, *J. Electron Spectrosc.* **3**, 263 (1979).
- [12] T. ABUAIN, I. C. WALKER and D. F. DANCE, *J. chem. Soc. Faraday Trans. II* **82**, 811 (1986).
- [13] P. V. KAMATH, M. S. HEGDE and C. N. R. RAO, *J. phys. Chem.* **173**, 1990 (1986).
- [14] M. C. DURRANT, M. S. HEGDE and C. N. R. RAO, *J. chem Phys.* **85**, 6356 (1986).
- [15] M. S. HEGDE, V. JAYARAM, P. V. KAMATH and C. N. R. RAO, *Pramana* **24**, 293 (1985).
- [16] V. JAYARAM and M. S. HEGDE, *Proc. Ind. Acad. Sci. (Chem. Sci.)* **97**, 617 (1986).
- [17] J. E. HUEHEY, *Inorganic Chemistry*, p. 842. Harper and Row, New York (1978).