SPIN-ORBIT RELAXATION OF HTe (X²Π₁/₂)

D. J. LITTLE and R. J. DONOVAN

Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 (Gt. Britain)

and R. J. BUTCHER

Department of Physical Chemistry, University of Cambridge, Lensfield Road, Cambridge (Gt. Britain)

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SUMMARY

Electronically excited $HTe(X^2\Pi_{1/2})$ radicals have been observed following the isothermal flash photolysis of H_2Te. Spin-orbit relaxation to the electronic ground state, $HTe(X^2\Pi_{3/2})$, has been monitored and the cross-section for relaxation by argon determined as $\sigma = (4.6 \pm 3.5) \times 10^{-20}$ cm². This value is significantly larger than that for the isoelectronic *atom* $I(5^2P_{1/2})$. The production of $HTe(X^2\Pi_{1/2})$ in the primary photochemical step is discussed within the context of a correlation diagram using double groups (groups in which spin is included in the total representation).

INTRODUCTION

While the spin-orbit relaxation of electronically excited atoms has been studied in considerable detail in recent years[1-4] little is known about the analogous process for molecules. The possibility of transferring electronic energy into vibrational and rotational energy of the initially excited molecule, during a collision, (*i.e.* collision induced *intra*molecular energy transfer) provides a number of channels for relaxation which are not available to excited atoms. These channels might therefore be expected to contribute to the total cross-section for quenching, and thus lead to significantly larger values than those typically found for atoms. However, it is interesting to note that despite the presence of these additional channels, electronically excited molecules may still be highly metastable to collisional relaxation, as evidenced by the extremely small cross-sections reported for quenching of $O_2(a^1\Delta_g)$ by a wide range of collision partners[5]. The only previous work on the spin-orbit relaxation of a molecule, of which the authors are aware, is that[6] for NO $(X^2\Pi_{3/2})$. The spin-orbit coupling energy in this case is 121 cm⁻¹ $(^2\Pi_{3/2}-{}^2\Pi_{1/2})$. Ultrasonic pulse techniques show[6] that spin-orbit relaxation is fast (16 $\pm$ 4 collisions with NO at 293 K) as expected for small excitation energies.

Spin-orbit relaxation of atoms has been studied more widely, notably with the alkali[1] and halogen atoms[2]. The latter have been of particular interest recently, due to their role in a number of photochemical laser systems (the iodine atom laser, reported by Pimentel *et al.*[7], was in fact the first photochemical laser to be described).

The HTe radical is isoelectronic with the iodine atom and thus spin-orbit relaxation,

$$HTe(X^2\Pi_{1/2}) + M \rightarrow HTe(X^2\Pi_{3/2}) + M + \Delta E(3840 \text{ cm}^{-1}) \tag{1}$$
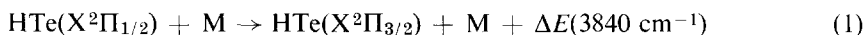
by various quenching gases (M) may be directly compared with the extensive data[2,8,9] for $I(5^2P_{1/2})$. We here report data for relaxation of $HTe(X^2\Pi_{1/2})$ by Ar; we intend to extend this study to include quenching by diatomic molecules at a later date.

EXPERIMENTAL

The apparatus employed for this study was of conventional design for flash photolysis with flash spectroscopy in the ultra-violet. The photoflash lamp and reaction vessel were constructed of Vitreosil quartz (Thermal Syndicate) and were likewise of conventional design (both 1 m in length and placed parallel inside a highly polished aluminium reflector). Flash energies of 1000 J were found to produce the required degree of photolysis; half life of flash $\tau_e = 20 \ \mu s$.

Spectra were recorded on Kodak Panchro Royal film (sensitized for short wavelengths by immersion in a saturated solution of sodium salicylate in ethanol) using a Hilger medium quartz spectrograph (E301).

H_2Te was prepared by the action of H_2O on aluminium telluride, and purified by low temperature vacuum distillation[11]. Mixtures of H_2Te with Ar were made up 1–2 h prior to use and later discarded if not entirely used in any given run. Under these conditions, very little decomposition of the H_2Te was found to occur. The partial pressure of H_2Te present in the reaction vessel was typically 2.7 N/m^2, with Ar pressures ranging from 1.3 to 13.3 kN/m^2, thus ensuring isothermal conditions (rate data are given for 293 K). After each flash the reaction vessel was immediately evacuated, thus reducing the rate of tellurium deposition in the vessel. However, despite these precautions it was still found necessary to clean the reaction vessel (5% HF solution was used) after 5 or 6 sets of experiments. Thus to minimize systematic effects, due to the slow build up of tellurium, in any one set, the delay times were arranged in a random sequence.

RESULTS AND DISCUSSION

Evidence has now been presented[10] for two primary photochemical channels in the ultra-violet photolysis ($\lambda > 190$ nm) of H_2Te, *viz.*:

$$H_2Te \xrightarrow{h\nu} H + HTe(X^2\Pi_{1/2,3/2}) \tag{2}$$

$$H_2Te \xrightarrow{h\nu} H_2 + Te(5^1D_2) \tag{3}$$

The relative importance of these channels is likely to vary with wavelength, but this dependence has not yet been established. Both $HTe(X^2\Pi_{1/2,3/2})$ and $Te(5^1D_2)$ have been observed directly[10,11], together with the three spin orbit components of the ground state atom[3] $Te(5^3P_{2,1,0})$. The latter are probably formed by secondary reactions between hydrogen atoms and HTe, or by secondary photolysis of HTe. Evidence from the present study, in which rapid decay of $HTe(X^2\Pi_{1/2})$ during the flash was observed, provides evidence for these proposals. However, the point of primary concern to this work, is the observation of $HTe(X^2\Pi_{1/2})$ in sufficient concentrations to allow kinetic studies.

The decay of this electronically excited radical after the flash ($t > 25\ \mu s$) is relatively slow (Fig. 1) and a plot of ln (optical density) ($\lambda = 218$ nm) against time

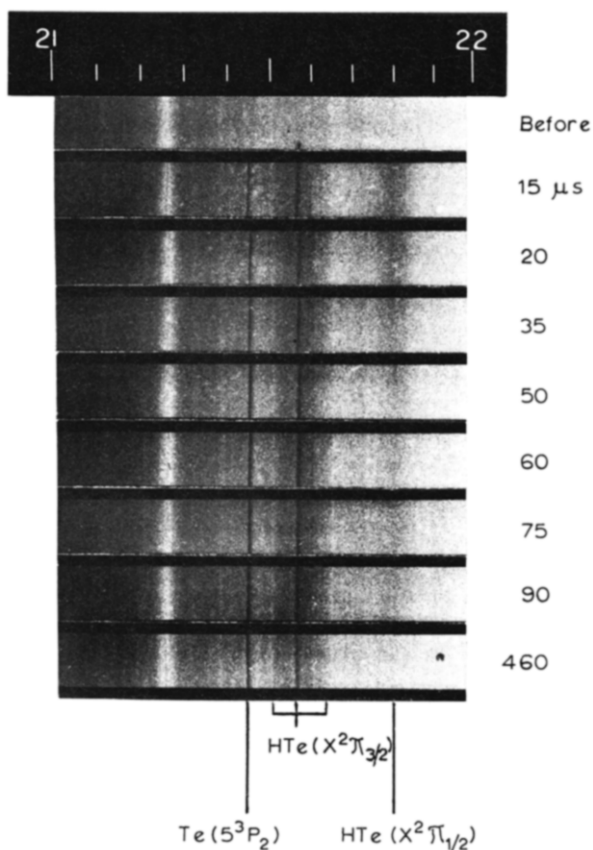Fig. 1. Decay of $HTe(X^2\pi_{1/2})$ in the presence of argon (delay times in μs; $P_{Ar} = 8.0$ kN/m²; $P_{H2Te} = 2.66$ N/m²; approximate wavelengths indicated by scale, 210–220 nm).

yields reasonable straight lines, indicating that the removal process may be characterized by a first order decay coefficient. The decay of $HTe(X^2\Pi_{1/2})$ is accompanied by a growth in the ground state $HTe(X^2\Pi_{3/2})$ concentration, showing that physical quenching, rather than chemical reaction, is the main channel for removal of the excited state. A comparison of the intensities of the spectra for $HTe(X^2\Pi_{1/2})$ and $HTe(X^2\Pi_{3/2})$ during the flash, indicates that a population inversion probably exists for a short period ($t < 20$ μs under the conditions used here).

Addition of a quenching gas to the system causes the rate of decay of $HTe(X^2\Pi_{1/2})$ to increase significantly, and data obtained for quenching by argon are presented in Fig. 2. These data yield a second order rate constant for quenching by argon of $k = (2.1 \pm 1.5) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}, which corresponds to a quenching cross-section of $(4.6 \pm 3.5) \times 10^{-20}$ cm^2; (errors are quoted for two standard deviations).

This small but finite value for the quenching cross-section is interesting, as it is at least a factor of 10^3 greater than that for quenching of $I(5^2P_{1/2})$ by Ar. However, it should be noted that the spin-orbit energies involved are significantly different; the spin-orbit splitting for $I(5^2P_{1/2})—I(5^2P_{3/2}) = 7603$ cm^{-1}, while the splitting for HTe is only 3840 cm^{-1}. A more reasonable comparison in terms of spin-orbit energy may be made with $Br(4^2P_{1/2})$ ($\Delta E = 3685$ cm^{-1}); it can be seen that relaxation of $HTe(X^2\Pi_{1/2})$ is at least a factor of ten more efficient than relaxation of $Br(4^2P_{1/2})$ ($k_{Ar} < 2 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1})^2. On the basis of this evidence it would appear that *intramolecular* energy transfer channels give rise to a significantly greater quenching cross-section for $HTe(X^2\Pi_{1/2})$, compared with the halogen atoms. This proposal is particularly attractive for relaxation of $HTe(X^2\Pi_{1/2})$, as the process:
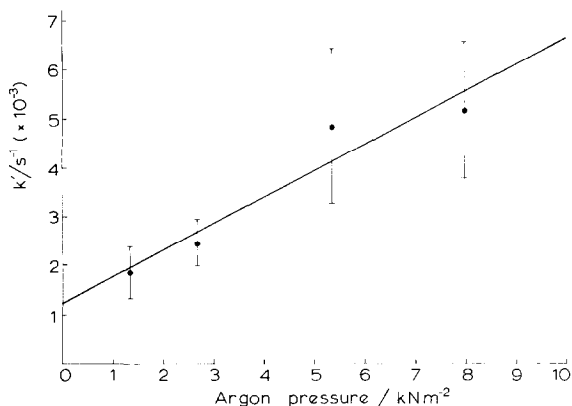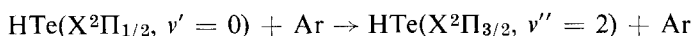
$$HTe(X^2\Pi_{1/2}, v' = 0) + Ar \rightarrow HTe(X^2\Pi_{3/2}, v'' = 2) + Ar$$

Fig. 2. Plot of first-order rate coefficients against pressure of added argon ($P_{H2Te} = 2.7$ N/m^2).

is close to being resonant $(\Delta E = 160 \text{ cm}^{-1})$. Thus the colliding argon atom would serve mainly to produce a perturbing field which mixes the initial and final states.

It should be noted that our failure to observe vibrationally excited HTe cannot be taken as evidence against intramolecular transfer, as unfavourable Franck–Condon factors for transitions from $v'' > 0$, would render the photographic techniques employed here too insensitive to detect such excitation. Rotational excitation would also go undetected with the present technique. It is clear therefore, that more sensitive direct techniques will be required to resolve the detailed aspects of this energy transfer process.

A more detailed discussion of the photochemistry of H_2Te will be given elsewhere; however, one point of significance to the present study concerns the high yield of $HTe(X^2\Pi_{1/2})$. The yield is surprisingly high, as the yield of $I(5^2P_{1/2})$ following the flash photolysis of HI (isoelectronic with H_2Te), is very low[12]. This might therefore suggest that $HTe(X^2\Pi_{1/2})$ is produced in a secondary reaction such as:

$$Te(5^1D_2) + H_2Te \rightarrow HTe(X^2\Pi_{1/2}) + HTe(X^2\Pi_{3/2}) \tag{5}$$

rather than the primary photochemical process. This may be ruled out, however, as the half-life of this reaction[10], under the conditions used, is $\sim 100 \ \mu s$ and could not therefore account for the observed rapid rate of production. Similarly, energy transfer from $Te(5^3P_{0,1})$ can be excluded as a recent investigation[3] shows that the rate of this process would also be too slow. The secondary reaction:

$$H + H_2Te \rightarrow HTe + H_2 \tag{6}$$

may also yield $HTe(X^2\Pi_{1/2})$, but the reaction,

$$H + HI \rightarrow H_2 + I \tag{7}$$

is known to yield predominantly ground state iodine atoms[13], $I(5^2P_{3/2})$, and it would therefore appear unlikely that reaction (6) is important.

We must thus consider the primary photochemical step in more detail. Figure 3(a) is a correlation diagram for the three lowest "known" states of H_2Te, with the products HTe and H, constructed using double groups. It has been assumed that the states of H_2Te have similar relative energies to those of H_2O, and only states which have been well established by spectroscopic or electron scattering studies[14] have been included. It is clear from Fig. 3(a), that excitation to the $\tilde{A}^1B_1$ state will yield $HTe(X^2\Pi_{3/2})$ and not the excited spin-orbit state as required. However, we note that one A' component of the $^3B_1$ state (Fig. 3a) does correlate with $HTe(X^2\Pi_{1/2})$. Remembering that the relatively intense ultra-violet continuum of HI arises from a singlet–triplet transition $(^3\Pi \leftarrow X^1\Sigma^+)$, it would appear plausible that a transition of comparable intensity would be present for H_2Te, coupling the states $(^3B_1 \leftarrow \tilde{X}^1A_1)$.
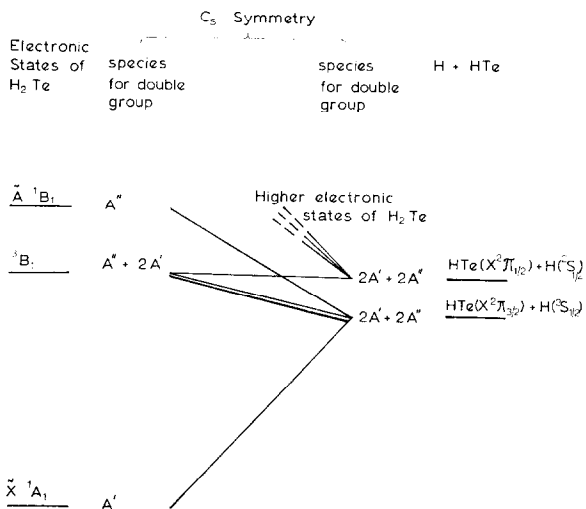
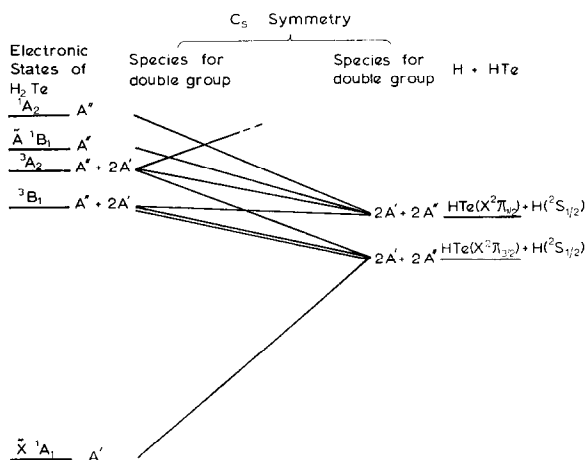Fig. 3(a). Correlation diagram for H_2Te dissociating to HTe + H.

Fig. 3(b). Correlation diagram for H_2Te dissociating to H + HTe, including the $^3A_2$ and $^1A_2$ states.

While the above proposals involving a transition to the $^3B_1$ state are compatible with the experimental observations, they do not support the tentative suggestion that a population inversion is produced in the spin-orbit multiplets of HTe (dissociation of the $^3B_1$ state would yield $^2\Pi_{1/2}/^2\Pi_{3/2}$ in the proportion 1:2, while population inversion requires a 1:1 ratio in this case). We must therefore ask whether there is any evidence for other low lying states of H_2Te which would modify Fig. 3(a). Turning again to H_2O for guidance on the relative ordering of low lying states, we find that there is theoretical and experimental evidence[14] for two more states in the relevant energy range, although their positions have not

been well characterized. These states are a $^1A_2$ state which probably lies just above the $\tilde{A}^1B_1$ state, and a $^3A_2$ state which lies above the $^3B_1$ state, but probably below $\tilde{A}^1B_1$. Figure 3(b) has been constructed to take account of these states. The presence of the $^3A_2$ state now requires that the $\tilde{A}^1B_1$ state correlates with HTe $(X^2\Pi_{1/2})$ and if absorption were exclusively *via* the transition $(\tilde{A}^1B_1 \leftarrow \tilde{X}^1A_1)$, then only electronically excited HTe radicals would be produced. It is more likely, however, that transitions to both the $^3B_1$ and $\tilde{A}^1B_1$ states will occur and result in a marginal population inversion of the spin-orbit states. It is clear that this argument depends on the $^3A_2$ state lying below the $\tilde{A}^1B_1$ state; independent theoretical and experimental data[14] support this proposal for H_2O (see ref. 14 for a discussion of this point). The $^1A_2$ state referred to above is unlikely to influence the primary photochemical step in any way. Thus transitions to this state from the ground state of H_2Te, are electronically forbidden, and although vibronically allowed, are expected to be weak.

The $^1B_1$ state of H_2Te also correlates with $H_2 + Te(5^1D_2)$ and the products of both reactions (2) and (3) may therefore result from excitation to this state.

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