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11-2012

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Abstract

The iso-polyhalomethanes are important reactive intermediates, displaying intense near-UV absorption bands that have been assigned to the $S_0 \rightarrow S_3$ transition on the basis of Time-Dependent Density Functional Theory (TDDFT) calculations. In this work, theory and multi-dimensional Franck–Condon (FC) analysis are used to model the electronic spectra of selected iso-polyhalomethanes. The $S_0 \rightarrow S_3$ transition approximately corresponds to a π–π^* transition on the halocarbocation subunit, which induces significant geometry changes. The calculated multimode FC profiles capture features of the experimental spectra of the matrix-isolated species, and are compared with the results of previous Resonance Raman studies of the isomers in solution.

Graphical abstract
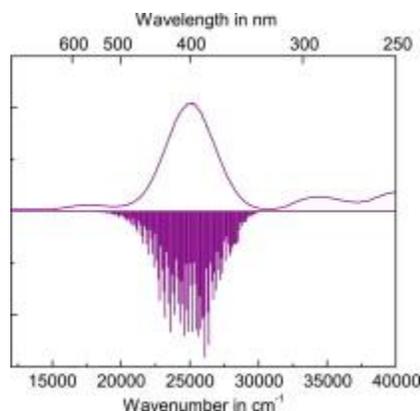
1. Introduction

The iso-polyhalomethanes are important reactive intermediates in the photochemical reactions of polyhalomethanes in both gas [1] and condensed phases [2], [3], [4], [5], [6], [7], [8], [9], [10], [11], [12], [13], [14], [15], [16], [17]. The bonding in the iso-species is dominated by ion–pair interaction between a halocarbocation and halide anion, and the isomerization reaction thus represents an electron transfer event. In condensed phases, these isomers are readily formed in the geminate recombination of the nascent radical pair formed following photolytic cleavage of the carbon-halogen bond in the parent halon. Building upon the initial matrix studies of Maier and co-workers [2], [3], [18], and subsequent studies in solution [4], [5], [6], [7], [8], [9], [10], [11], [12], [13], we have recently examined the vibrational and electronic spectroscopy of a series of iso-polyhalomethanes in cryogenic matrices [1], [14], [15], [16], [17], [19]. Recently, in collaboration with groups at UW-Madison, we have probed on the ultrafast timescale the formation and vibrational relaxation of iso-CH_2ClI in solution and cryogenic matrices [17]. In agreement with earlier time-resolved Resonance Raman (RR) studies of the formation and relaxation of iso-polyhalomethanes in solution [8], this study found characteristic and environmentally invariant timescales of ~1–2 ps for isomer formation and ~50 ps for vibrational relaxation of the hot isomer into its potential well.

The electronic spectra of the iso-polyhalomethanes universally exhibit a broad, very intense absorption band in the near-UV to Visible region, with weaker band(s) lying at lower energy [2], [3], [15], [16], [18]. On the basis of Time-Dependent Density Functional Theory (TDDFT) calculations, we have assigned the strong feature to the $S_0 \rightarrow S_3$ transition, with the overlapping $S_0 \rightarrow S_1$, S_2 transitions lying to lower energy [15], [19]. The calculated oscillator strength of the $S_0 \rightarrow S_3$ feature is in good agreement with experiment, while the $S_0 \rightarrow S_1$, S_2 absorptions are calculated to be much weaker than observed experimentally, suggesting that these bands borrow intensity from the $S_0 \rightarrow S_3$ transition.[16] In both ultrafast transient absorbance and RR experiments, the intense $S_0 \rightarrow S_3$ absorption has been used to probe the formation and decay of the isomer [4], [5], [6], [7], [8], [9], [10], [11], [12], [13], [17], yet no studies to date have examined the nature of this absorption, or attempted to model the electronic spectrum. In this Letter, we report the first modeling of the electronic absorption spectrum of the iso-halons, using theory in concert with multidimensional Franck–Condon simulations. Our data are compared with previous RR experiments that probed the spectroscopy of the isomer at selected wavelengths within the $S_0 \rightarrow S_3$ absorption band.[4], [8]

2. Experimental and computational methods

The details of the experimental approach have been previously described in detail [15], [16]. Briefly, samples of polyhalomethanes in Ar or Ne at typical mixing ratios of 1:1000 were prepared by passing high purity Ar or Ne gas at a typical pressure of 3 bar over the chemical held in a temperature controlled bath. In some cases, mixtures were premade in a stainless steel mixing tank using standard manometric techniques. The mixture was deposited onto the cold window held at ~5 K using a solenoid actuated pulsed valve; typical conditions were: 1 ms pulse duration, 10 Hz repetition rate, 1 h deposition time, 1 bar backing pressure.

Following deposition, the cold window was irradiated with UV laser light from the frequency doubled output of a dye laser system (Lambda-Physik Scanmate 2E), pumped by the third harmonic (355 nm) of a Nd:YAG laser (Continuum NY-61). The photolysis beam was expanded using a 4:1 beam expander to fill the cold window and avoid damage to the cryostat windows [20]; typical irradiation times were 1 h at 10 Hz, with 0.5 mJ/pulse. Infrared (IR) absorption spectra were recorded with a Thermo Nicolet NEXUS series FTIR at typically 1–2 cm^{-1} resolution and averaged over 128 scans. Ultraviolet/visible (UV/VIS) absorption spectra were obtained with an Agilent 8453 diode array spectrophotometer. The reference spectra for both IR and UV/VIS were recorded for the cold sample holder immediately prior to matrix deposition, and the entire cryostat was mounted on a home-built rail system that allowed quick interchange between spectrometers. All spectra were transferred to a spreadsheet and analysis program (Origin 8.0) for subsequent workup.

Calculations were carried out using the Gaussian 09 [21] and NBO 5.9 [22] programs on the MU Pere cluster. Geometry optimization was performed using DFT and TDDFT (CAM-B3LYP and TDCAM-B3LYP) methods with correlation consistent basis sets, typically aug-cc-pVTZ [23], [24], [25], [26]. For Iodine, Peterson's effective core potential basis (aug-cc-pVTZ-pp) was used [27]. Time-dependent DFT (TDDFT) methods are now widely used for modeling electronically excited states, and it is well appreciated that local exchange functionals perform poorly for states involving significant charge transfer [28]. Thus, in this work we employed the CAM-B3LYP functional, which has previously been shown to model well the electronic spectrum of the iso-halons [16], [19]. The vibrational frequencies and mass-weighted displacements (*l*-matrices) derived from the (TD) DFT calculations were used as input into a multidimensional Franck–Condon routine in the PGOPHER program suite [29], which incorporated the full effects of Duschinsky mixing.

3. Results and discussion

Figure 1 shows examples of the electronic spectra of matrix isolated iso-polyhalomethanes measured in our lab in cryogenic (Ar or Ne) matrices at 5 K, following photolysis of the parent halon. All spectra show weak ($S_0 \rightarrow S_1$, S_2) transitions in the visible and a much stronger ($S_0 \rightarrow S_3$) transition lying in the near-UV region of the spectrum. These bands are uniformly broad, with Full Width at Half-Maxima (FWHM) of several thousand cm^{-1}, and are featureless. The calculated (TDCAM-B3LYP/aug-cc-pVTZ, with aug-cc-pVTZ-pp basis set for I) electronic absorptions of these species are given in Table S1 in the supporting information.
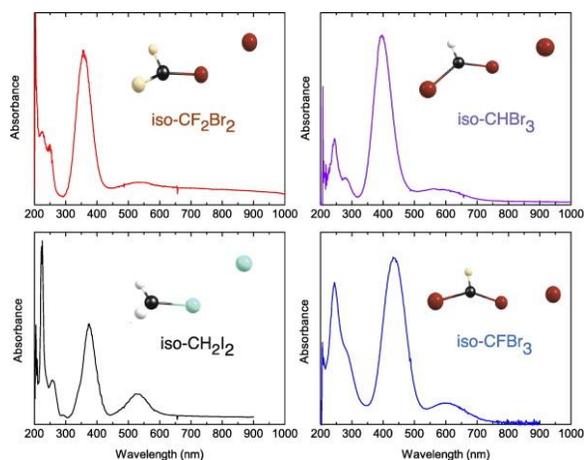
Figure 1. Example UV–Visible spectra of iso-polyhalomethanes trapped in rare gas cryogenic matrices at 5 K. From upper left: iso-CF_2Br_2 (Ar), iso-$CHBr_3$ (Ne), iso-$CFBr_3$ (Ne), iso-CH_2I_2 (Ar). All species show weak $S_0 \rightarrow S_1$, S_2 absorptions peaking in the visible, and a stronger ($S_0 \rightarrow S_3$) absorption in the near-UV/blue region. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Focusing first on iso-$CHBr_3$, the structures of the S_0 and S_3 states were optimized at the (TD)CAM-B3LYP/aug-cc-pVTZ level, and the optimized structures and selected geometrical parameters are shown in Figure 2. It is immediately seen that electronic excitation induces large structural changes. Most notably, in the excited state the C–Br bond length increases by ~0.1 Å, the Br–Br bond length increases by ~0.4 Å, and the C–Br–Br bond angle increases by ~54°. To understand these changes, we consider that the $CHBr_2^+$ subunit can be described by two different types of resonance structures: (1) structures containing a C = Br double bond, where the positive charge is localized on the doubly bonded Br atom, and (2) a structure containing all single bonds where the positive charge resides on the central C atom (Figure S1). As shown in Figure S2, the electronic transition, which TDDFT calculations indicate is largely described by a simple HOMO–LUMO excitation, resembles a π–π* excitation on the $CHBr_2^+$ 'chromophore'. Thus, excitation weakens the C–Br bond and, in producing a greater positive charge density on the central C atom, should also weaken the Br–Br interaction.
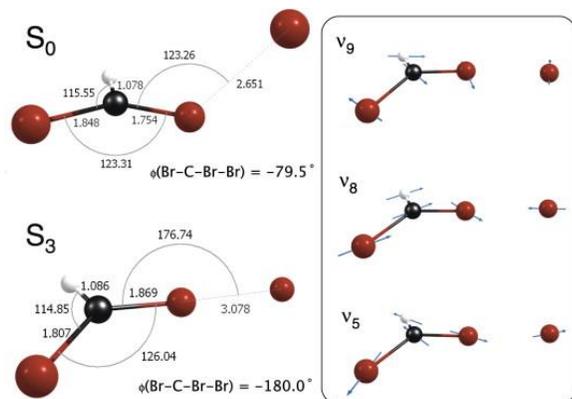

Figure 2. Optimized structures of the S_0 and S_3 states of iso-$CHBr_3$. The prominent Franck–Condon active modes are shown at right.

Consistent with this picture, the modes displaying the largest displacements in the electronic transition, as illustrated in Figure 2, are v_5 (symmetric C–Br stretch), v_8 (Br–Br stretch), and v_9 (torsion). The frequencies of these modes in the $S_0(S_3)$ states are (in cm^{-1}): v_5 = 618(536), v_8 = 175(127), and v_9 = 49(48); the complete set of calculated frequencies in the two electronic states are provided in Table S2 in the supporting information. Our findings are consistent with earlier time-resolved Resonance Raman (RR) spectra of Phillips and co-workers,

taken at a probe wavelength of 435.7 nm in cyclohexane solution, which show the strongest activity in v_8, with activity also observed in v_3, v_4, v_5, and v_6 [4]. In the RR studies v_9 could not be observed due to its low frequency; however, we note that the band at 214 cm^{-1} assigned to the v_6 fundamental lies also near the predicted position of the $v_8 + v_9$ combination. The calculated frequencies and mass-weighted displacements were included in the Franck–Condon (FC) simulation, taking into account the effects of Duschinsky mixing.

Figure 3 shows a comparison of the experimental data for the $S_0 \rightarrow S_3$ transition in iso-CHBr$_3$ with the results of a three-mode FC simulation, incorporating transitions in v_5, v_8, and v_9. A diagonal anharmonicity constant equal to 1% of the harmonic frequency was assumed for each mode, and only transitions from the vibrationless level of S_0 were considered, as this should be the only level populated under our experimental conditions. The simulated spectrum is shown as a stick spectrum in Figure 3, in order to illustrate the large density of vibrational bands in the FC envelope. The lack of structure in the experimental spectrum can be attributed to two other factors: (a) the low resolution of the experimental spectrum (ca. 1 nm or ~60 cm^{-1} at λ_{max}), and (b) broadening due to the matrix environment, which can be substantial, particularly for ionic structures [30], [31]. Indeed, adding a Gaussian linewidth of ~150 cm^{-1} to the spectrum shown in Figure 3 is sufficient to wash out all vestiges of vibrational structure. Of course, we cannot rule out a homogeneous contribution to the linewidth – indeed, excitation into the S_3 band is known to regenerate the parent molecule through a mechanism (photoisomerization or dissociation followed by geminate recombination) that has not been established.
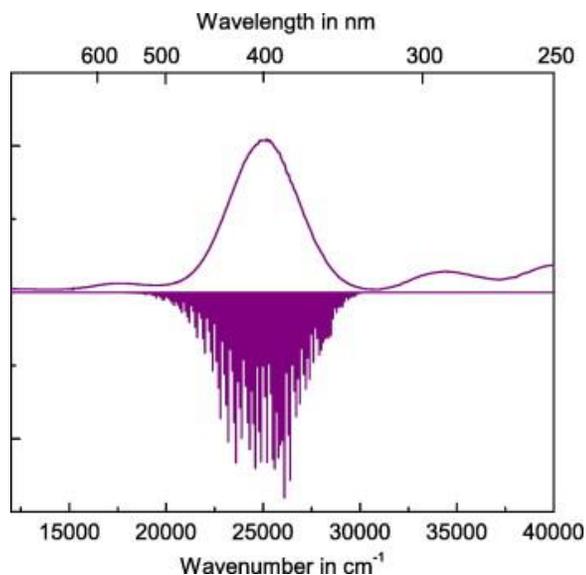

Figure 3. Experimental (top) and Franck–Condon simulation of the $S_0 \rightarrow S_3$ transition of iso-CHBr$_3$. The simulation included three modes, as described in the text, and is shown as a stick spectrum to illustrate the density of transitions.

Based upon input from theory with no adjustable parameters, the simulation shown in Figure 3 captures many features of the experimental spectrum. Importantly, it shows that the width of the experimental spectrum arises primarily from the pronounced FC envelope, due to large structural changes in the electronic transition. In order to corroborate these findings, we modeled the electronic spectra of other iso-polyhalomethanes. As another example, shown in Figure S3 are optimized structures of the S_0 and S_3 states of iso-CH$_2$Br$_2$ at the (TD)CAM-B3LYP/aug-cc-pVTZ level. Overall, the structural changes upon electronic excitation are similar to those observed for iso-CHBr$_3$, as the dominant component to the transition again is a single electron promotion from HOMO to LUMO, roughly characterized as a $\pi–\pi*$ transition localized on the CH$_2$Br$^+$ chromophore. Upon electronic excitation, the C–Br–Br bond angle increases by some 60°, while the Br-Br bond length increases by 0.85 Å. Our analysis shows that the A′ modes showing the largest FC activity are: v_3 (C–Br stretch), v_5 (Br–Br stretch) and v_6 (C–Br–Br bend). The frequencies of these modes in the $S_0(S_3)$ states are (in

cm^{-1}): v_3 = 903(1113), v_5 = 193(184), and v_6 = 142(84). Consistent with this finding, the time-resolved RR spectra of Phillips and co-workers, taken at a probe wavelength of 341.5 nm in cyclohexane solution, show the strongest activity in v_5, with activity also observed in v_6 [4]. The frequency range of the reported RR data for iso-CH_2Br_2 did not encompass the fundamental of v_3; however, the v_3 fundamental was observed in RR spectra of a related system, iso-CH_2I_2 [4].

The calculated [(TD)CAM-B3LYP/aug-cc-pVTZ] vibrational frequencies in the S_0 and S_3 electronic states of iso-CH_2Br_2 are given in Table S1 in the supporting information, and the data from these calculations were input into the FC simulation. Figure 4 shows a comparison of experimental data for the $S_0 \rightarrow S_3$ transition in iso-CH_2Br_2 with the results of a three-mode FC simulation incorporating transitions in v_3, v_5, and v_6. Again, a diagonal anharmonicity constant equal to 1% of the harmonic frequency was assumed for each mode, and only transitions from the vibrationless level of S_0 were considered. The simulated spectrum is shown as a stick spectrum, as before. The FC simulation again captures the salient features of the experimental spectrum, including the observed asymmetry and pronounced width of the absorption feature, which has a FWHM of ~3600 cm^{-1}. As above, the lack of vibrational structure in the experimental spectrum indicates significant inhomogeneous broadening from the matrix environment and/or homogeneous broadening.
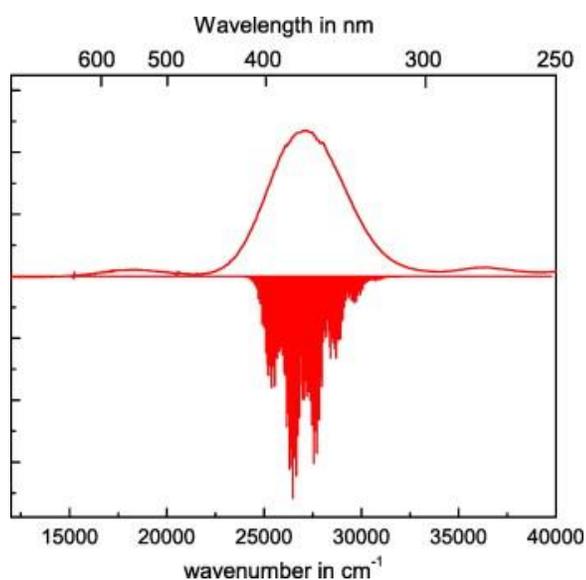

Figure 4. Experimental (top) and Franck–Condon simulation of the $S_0 \rightarrow S_3$ transition of iso-CH_2Br_2. The simulation included three modes, as described in the text, and is shown as a stick spectrum to illustrate the density of transitions.

4. Conclusions

We have examined the electronic spectroscopy of the iso-polyhalomethanes through a combination of theory and Franck–Condon analysis, which were compared with experimental data on the matrix-isolated species. In agreement with experiment, TDDFT calculations show that the spectra are dominated by a strong $S_0 \rightarrow S_3$ transition, which is roughly described as a π–π^* transition on the halocarbocation subunit. The optimized structure of the S_3 state shows that large geometry changes occur upon electronic excitation, particularly in the C–Br–Br angle and Br–Br bond length, which induces significant FC activity in the corresponding vibrational modes. Our simulated spectra using a multidimensional FC analysis based upon the theoretical parameters capture many features of the experimental spectra, and are consistent with previous RR experiments in solution. As a further probe of our findings, it would be particularly informative to measure RR spectra and excitation profiles of matrix-isolated iso-polyhalomethanes, and experiments to that end are planned.

Acknowledgements

Appendix A. Supplementary data

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Supplementary data.

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