Photodissociation Dynamics and Stereodynamics of Methyl Mercaptan and Dimethylsulfide from the Second Absorption Band at 201 and 210 nm

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Abstract

The role of promoting and spectator modes *vs.* energy randomization in non-adiabatic dynamics is interrogated in the photodissociation of methyl mercaptan, CH₃SH, and dimethyl sulfide, CH₃SCH₃ or DMS, in the second absorption band. The primary

CH₃(ν) radicals produced in the dissociation of both systems at 210 nm have been resonantly detected in slice-imaging experiments and the corresponding translational energy and angular distributions have been obtained. The stereodynamical information provided by Dixon’s bipolar moments in conjunction with the energy partitioning among the different degrees of freedom of the primary CH₃(ν) products offers a panoramic picture of the photodissociation process of both systems. The remarkable similitude found between the two systems related to both vector correlations and internal energy content of the corresponding counterparts — SH for methyl mercaptan and SCH₃ for DMS — indicates that despite the diabaticity of the process, no efficient energy randomization of the available energy takes place. More specifically, only the parent vibrational modes whose participation in the initial absorption step is imposed by the conical intersection — *i.e.* the promoting modes — are adiabatically preserved during the process, while the rest of the vibrational modes play the spectator role. The results for both molecules at 210 nm are complemented with experiments carried out for DMS at 201 nm to explore the internal mechanism of the conical intersection in different zones of the absorption region.

Introduction

Photodissociation of substituted dihydrogen sulfides R₁-S-R₂ (where R₁ and R₂ denote either a hydrogen atom or a hydrocarbon chain) in the second absorption band is governed by an interesting prototypical dynamics which starts in the excitation step. These systems are examples of the role of non-nadiabatic interactions in photodissociation through their influence on the superposition of electronic states initially prepared. Such effect becomes particularly evident in systems where the region of electronic non-adiabaticity occurs in the Franck-Condon region while absorption to one of the electronic states is only allowed vibronically *i.e.*, it is electronically forbidden by symmetry.

Methyl mercaptan, CH₃SH, and the double methyl substituted analog, dimethyl sulfide

(DMS), CH_3SCH_3 , have been used as testing grounds to assess the role of same symmetry conical intersections in photodissociation dynamics.^{1,2} The UV electronic spectrum of CH_3SH shows two absorption bands, a broad band centered around 235 nm – the *A*-band – and a more intense transition centered around 204 nm, the *B*-band. Absorption around 210 nm, the wavelength employed in the present work, leads ground state CH_3SH ($\tilde{X}^1A'$) molecules to the $2^1A''$ second excited state. The bound $2^1A''$ state, unlike the lower energy dissociative $1^1A''$ state, does not correlate adiabatically with ground state $\text{CH}_3(\tilde{X}^2A'')$ and $\text{SH}(X^2\Pi)$ products. Dissociation in this state is produced, therefore, through a seam of conical intersections between the $2^1A''$ and the dissociative first excited state $1^1A''$ strategically located in the Franck-Condon absorption region. Computational determination of the conical intersection (CI) seam shows that on the interaction surface the C-S and S-H coordinates are strongly coupled. Furthermore, the conical intersection seam can be sufficiently characterized using a two parameter model, involving simultaneous C-S and S-H stretch.

The effect of non-adiabaticity on photoabsorption is for DMS, as for the rest of double-substituted sulfides, even more dramatic. The two low-lying electronic states in these systems, 1^1B_1 and 1^1A_2 , are energetically accessible from the ground $\tilde{X}^1A_1$ state^{3,4} although only the $1^1B_1 \leftarrow \tilde{X}^1A_1$ transition is electric-dipole allowed in the limit of C_{2v} symmetry. Small distortions from the C_{2v} geometry due to excitation of the C-S-C asymmetric stretch, which happens necessarily in the first steps of the dissociation process, causes a lowering of molecular symmetry to C_s , enabling absorption between 210 and 190 nm, producing the second absorption band. In this scenario, the 1^1B_1 and 1^1A_2 states become $1^1A''$ (dissociative) and $2^1A''$ (bound) respectively, and are both accessible via electric dipole allowed transitions from the ground state. As in the case of methyl mercaptan, the bound $2^1A''$ state does not correlate adiabatically with ground state products and dissociation into $\text{CH}_3(\tilde{X}^2A'')$ and $\text{CH}_3\text{S}(\tilde{X}^2E)$ fragments takes place in the $1^1A''$ state due to the vibrational coupling between both $1^1A''$ states in the region of conical intersections within the Franck-Condon region of the one-photon absorption. Similar calculations than those performed for methyl

mercaptan show that a seam of conical intersections is formed in the C-S coordinate. The C-S bond stretching and distortion of the CH₃ and C-S-C bond angles appear to be the single coordinates relevant in the characterization of the seam. In other words, electronic excitation of DMS, — a C_{2v} molecule — in the second absorption band takes place to a seam of conical intersections *created* by the vibrational superposition of the first two C_s dipole allowed electronic states. The similarities between both systems become more striking when the differences are accounted for: while for CH₃SH the C-S distance increases markedly with the S-H bond stretch, the C¹-S and S-C² coordinates in DMS are not connected, truncating the possibilities of simultaneous 3 body fragmentation.

The CH₃($\tilde{X}^2A''$) + SH($X^2\Pi$) photodissociation channel of methyl mercaptan has been widely investigated in the first and second absorption bands using the velocity map imaging technique.⁵⁻⁷ Inverted vibrational populations of the SH co-fragment are extracted from the analysis of the measured CH₃(ν) translational energy distributions, highlighting the state-to-state character of the dissociation process. The absorption step from the ground CH₃SH($\tilde{X}^1A'$) to the $2^1A''$ state possesses perpendicular character resulting in a dissociation anisotropy parameter β close to the limiting value of -1 for dissociation on a pure repulsive surface. Not having found experimental signs of photofragment alignment, to the best of our knowledge, there is no literature on vector correlations of the photodissociation of methyl mercaptan.

In a set of early experiments carried out by our group,⁸⁻¹⁰ velocity map ion imaging experiments explored the photodissociation of DMS in a broad interval of wavelengths ranging from 231 nm (red edge of the first absorption maximum) down to 215 nm (already deep within the band). Dynamical differences and, in particular, possible non-adiabatic effects were expected to be revealed through the scan of the photolysis wavelength. A systematic comparison between the photodissociation of the two isotopomers DMS and DMS-d₆ was performed using resonance enhanced multiphoton ionization (REMPI) detection of the methyl fragments and non-resonant multiphoton ionization (MPI) measurements of methyl fragments in all ν vibrational states. The results showed that approximately a 70-80% of

the available energy in the photodissociation process is channeled into recoil energy. Furthermore, the recoil energy distributions showed that the available energy channeled into translation of the fragments decreases as the excitation energy of the parent molecule increases, which is an indication that the internal energy of the methylthio fragment increases as the photolysis wavelength decreases. Those results were rationalized in terms of a hybrid statistical-impulsive dissociation model.⁸

The analysis of the dissociation anisotropy of DMS provided β parameters close to the limiting value of -1 (for a pure perpendicular transition) while the full μ - v - J vector correlation analysis, *i.e.* the correlation between the transition dipole moment μ , the fragment recoil direction v , and the total angular momentum J of the detected fragment, indicated that the J vector does not have cylindrical symmetry about the recoil velocity v .^{8,9} Such result is in disagreement with a pure impulsive model, which considers only in-plane and out-of-plane rocking modes. It was suggested that the parent ν_3 C-S-C deformation mode, tentatively introduced in the hybrid model, could explain the alignment of the J vector.

In a rather recent work, the photofragment excitation (PHOFEX) spectroscopy technique was used to obtain the vibronic spectra of DMS and several deuterated isotopomers.¹¹ The PHOFEX spectra of the $\text{CH}_3(\nu=0)$ product, resonantly detected while the photolysis laser was scanned between 220 and 232.5 nm, showed vibrational activity in the C-S-C bending (ν_3), C-S-C symmetric stretch (ν_4) and in the in-plane CH_3 rocking (ν_9) modes. A lifetime of ~ 100 fs for the DMS excited state was obtained through the fit of the individual vibronic bands to Lorentzian profiles. In extraordinary agreement with the work of Aoiz and co-workers,⁸ the translational partitioning ratio was found to decrease with the excitation energy.¹¹ The authors suggest, however, that the short lifetime of ~ 100 fs makes unrealistic a statistical contribution to the dissociation process. Furthermore, the specific mode effect on the dissociation yield, attributed to the coupling of certain vibrational modes of the parent DMS to the reaction coordinate, should not be observed if the vibrational excitation were randomized before the bond cleavage.

The comparison between the photodissociation of CH_3SH and CH_3SCH_3 presented in this work aims to clarify the internal interplay of the conical intersection. To that end, the photodissociation of CH_3SH and CH_3SCH_3 at 210 nm (roughly the onset of the second absorption band) is interrogated and characterized through detection of the CH_3 primary and secondary dissociation fragments. The combination of the slice-imaging and REMPI techniques provide valuable information of the energy partitioning among the CH_3 , CH_3S and SH species as well as the means to extract the stereodynamical facts of the process. The coalescence of the energy and stereodynamics data provide a thorough picture of the role of promoting modes *vs.* spectator modes in prompt photodissociation processes mediated by conical intersections. The 210 nm results are complemented with photodissociation experiments on DMS at 201 nm to clarify the extent of the non-adiabaticity effect along the Franck-Condon region.

The paper is organized as follows: the most relevant results of the study are presented in Sec. III and discussed in Sec. IV, after a brief overview of the experimental set-up is given in Sec. II. Final conclusions are drawn in Sec. V.

Experimental section

The setup employed in the slice imaging experiments has been described in detail previously,^{12,13} and only a brief description is presented here. The whole experiment runs at a repetition rate of 10 Hz. A molecular beam is created by expanding a gas mixture of methyl mercaptan or DMS in He (10%, 1 atm backing pressure) into vacuum using a pulsed nozzle (General Valve Series 9, 0.5 mm orifice). The gas pulse is skimmed and collimated (Beam Dynamics, Standard Model 2, 0.5 mm diameter orifice) and reaches the ionization chamber where the already formed molecular beam is intersected at right angles, in the middle of the electrical plates of a time-of-flight (TOF) mass spectrometer, by the photolysis and the probe laser pulses, which are focused ($f=25$ cm) and counter propagated to each other.

Excitation of the parent species is carried out at 210 nm (DMS and CH₃SH) and 201 nm (DMS) generated using a sum-frequency mixing nonlinear crystal in combination with the fundamental and second harmonic radiation of a Nd:YAG (Quanta Ray Pro 230) pumped frequency doubled dye laser (Sirah Cobra-Stretch). The produced CH₃ fragments are ionized with a focused probe pulse generated by a Nd:YAG laser (Spectra-Physics Pro Series 450) pumped frequency doubled dye laser (Sirah Cobra-Stretch) delayed 10 ns with respect to the photolysis pulse. The probe wavelength was set at 333.45 nm, 333.9 nm and 329.5 nm for (2+1) REMPI detection of CH₃($\nu=0$), CH₃($\nu_1=1$) and CH₃($\nu_2=1$), respectively.

The generated CH₃⁺ ions are projected onto the position-sensitive detector system constituted by two microchannel plates (MCPs) coupled to a phosphor screen. Slice images of CH₃⁺ are recorded using a 500 ns extraction delay applied to the repeller plate and an effective 10 ns detector gate on the front MCP. Ion images are recorded using four laser polarization configurations, $X(\text{pump})X(\text{probe})$, XZ , ZX , and ZZ , where X is the direction perpendicular to the laser propagation axis (Y) (and parallel to the detector plane), and Z is parallel to the molecular beam (and parallel to the detector plane). The recorded slice images are quadrant-symmetrized prior to extracting the kinetic energy and angular distributions. The slice images are calibrated using the translational energy distributions (TEDs) of CH₃($\nu=0$) fragments from the well-known CH₃I photodissociation at 333.45 nm.

Results

Photodissociation of CH₃SH and CH₃SCH₃ at 210 nm

CH₃(ν) sliced images obtained after photodissociation of methyl mercaptan and dimethyl sulfide at 210 nm were recorded and analyzed. Appropriate balance of the different energy contributions provides a clear identification of the participating processes. For the primary dissociation channel, the center-of-mass translational energy E_T of the methyl fragments CH₃(ν) is calculated as follows:

$$E_T(\text{CH}_3(\nu)) = \frac{m_{\text{SR}}}{m_{\text{CH}_3\text{SR}}} [h\nu - D_0 + E_i(\text{CH}_3\text{SR}) - E_i(\text{SR})] \quad (1)$$

with $R = \text{H}$ or CH_3 . The frequency of the photolysis laser is represented by ν ; D_0 is the dissociation energy of the C-S bond (3.16 eV and 3.25 eV for CH_3SH and DMS , respectively^{5,14}), m_i are the masses and $E_i(\text{CH}_3\text{SR})$ and $E_i(\text{SR})$ refer to the internal energy of the parent and co-product species, respectively. The available energy marks included in the fragment translational energy distributions (see below) denote available energies, *i.e.*, translational energy E_T values correlating with zero internal energy of the co-products. The vibrational combs at the top of the right-side part of the translational energy distributions are calculated including in Eq. (1) the indicated vibrational mode of the SH or SCH_3 co-product.

According to Eq. (1), the portion of the translational energy distribution (TED) comprised at energies below the available energy label corresponds to internal energy transferred in the process to the photofragments, while the portion at higher energies reflects the contribution from parent molecules with internal energy. Whereas in molecular beam experiments, the internal energy of the parent molecule is supposedly low (the rotation to translation transfer is rather efficient and only certain vibrational excitation should be considered), in the estimation of the translational energy of secondary CH_3 fragments, the internal energy of the co-fragment CH_3S must be considered. The energy balance for the secondary dissociation process is given by:

$$E'_T(\text{CH}_3) = \frac{m_{\text{S}}}{m_{\text{CH}_3\text{S}}} [h\nu' - D'_0 + E_i(\text{CH}_3\text{S}) - E_i(\text{S})] \quad (2)$$

where ν' is the laser frequency (photolysis or probe) involved in the secondary photodissociation process, D'_0 is the S- CH_3 bond energy and $E_i(\text{CH}_3\text{S})$ and $E_i(\text{S})$ refer to the internal energy of the CH_3S produced in the primary dissociation and to the internal (electronic) energy of the sulfur atom obtained in the secondary dissociation, respectively.

The internal energy of the CH_3S product is solved from Eq. (1) as:

$$E_i(\text{CH}_3\text{S}) = h\nu - D_0 + E_i(\text{CH}_3\text{SR}) - \frac{m_{\text{CH}_3\text{SR}}}{m_{\text{CH}_3\text{S}}} E_T(\text{R}) \quad (3)$$

In Eq. (3), $E_T(\text{R})$ represents the R co-fragment translational energy distribution from the primary dissociation, and the term $E_i(\text{CH}_3\text{S})$ ranges from zero, if all the available energy in the primary dissociation process is assumed to be transferred into translational energy of the fragments, to the total available energy for the process, if the fragments are assumed to be formed with zero internal energy.

Figure 1 shows a series of XX sliced images corresponding to the formation of CH_3 in different vibrational levels (vibrationless $\nu=0$ and one quantum of excitation in the symmetric stretch mode ν_1 and in the umbrella mode ν_2) after excitation of methyl mercaptan at 210 nm. Three features showing different recoils and structures are observed in all cases. The outer anisotropic ring corresponds to the primary C-S dissociation channel and the associated well resolved structure correlates with the co-fragment SH vibrational distribution. The inner, broad and as well anisotropic ring, corresponds to the secondary dissociation channel of the hot CH_3S primary product into CH_3 and S fragments. The central blot is assigned to multiphoton dissociative ionization of the parent CH_3SH .⁷

Angular integration of the images shown in Figure 1 yields the translational energy distributions (TEDs) depicted in Figure 2. The three observed features, which are recovered in the distributions, show different functionalities and ratios. While the central blot shows, as expected, a Boltzmann-type profile, the primary dissociation distributions show a clearly resolved structure assigned to the vibrational distribution of the SH co-fragment. In the case of the secondary dissociation distribution, no clear structure is observed considering the three possible J states of the $\text{S}(^3P_{0,1,2})$ co-fragment and the blurring introduced by the internally excited CH_3S fragments produced in the primary dissociation.

The vertical bars, which designate the threshold for the primary and secondary (assuming excitation of hot CH_3S by a probe photon) dissociation processes, and the combs which indicate the vibrational progression of the correlating SH co-fragment and the J states of

Figure 1: $\text{CH}_3(\nu)$ XX sliced images obtained after photodissociation of CH_3SH at 210 nm. (a) $\text{CH}_3(\nu=0)$, (b) $\text{CH}_3(\nu_1=1)$ and (c) $\text{CH}_3(\nu_2=1)$.

$S(^3P_J)$, are calculated according to Eqs. (1)-(3). Contribution from internally excited CH_3SH parent molecules does not seem to be significant in the present case.

To extract the correlated vibrational distribution of the SH co-product, a simulation of the energy distribution was carried out. Each rotational peak was simulated using Gaussian lineshapes centered at the values of the S-H vibrational progression in the CM CH_3 translational energy space (Eq. (1)). A single fitting parameter was used to reproduce the width of all contributions, which reflects the instrumental function and the rotational temperature (Boltzmann rotational distributions were assumed), while the individual intensities were varied to obtain the relative populations. The fitting functions are also shown in Figure 2 and the extracted populations are plotted in Figure 3.

Figure 2: CH_3 center-of-mass (CM) translational energy distributions obtained by angular integration of the images shown in Figure 1 for (a) $\text{CH}_3(\nu=0)$, (b) $\text{CH}_3(\nu_1=1)$ and (c) $\text{CH}_3(\nu_2=1)$. The vertical bar at ~ 1.75 eV indicates the available energy for the primary photodissociation process. The combs depicted in the contribution arising from the primary dissociation represent the vibrational distribution of the co-fragment S-H bond stretching and the Gaussians with different colors correspond to the global fit of the distribution, each one for a given vibrational quantum number of $\text{SH}(\nu)$. The vertical bars depicted in the contribution from the secondary dissociation, *i.e.* dissociation of hot CH_3S after absorption of one probe photon, represent the $J = 0$ state of the $\text{S}(^3P_J)$ co-fragment when considering negligible internal energy for the CH_3S (solid) or the internal energy acquired by CH_3S in the primary dissociation process (dashed).

The SH vibrational distribution in correlation with $\text{CH}_3(\nu=0)$ has been studied in detail in former works carried out by Bañares and co-workers^{5,6} between 202 and 210 nm, and at 204 nm by Parker, Yang and co-workers⁷ who extended the analysis to ν_2 (umbrella) vibrationally excited methyl fragments. To the best of our knowledge, this is the first report on the correlation between the SH vibrational distribution and ν_1 (C-H symmetric stretch) excited CH_3 . In excellent agreement with the mentioned works,⁵⁻⁷ the SH vibrational distributions are inverted for the three measured vibrational states, a consequence of the forces involved in the conical intersection. Vibrationless methyl fragments correlate with a SH vibrational

Figure 3: Vibrational distributions of the SH co-fragment in correlation with $\text{CH}_3(\nu=0)$ (black), $\text{CH}_3(\nu_1=1)$ (red) and $\text{CH}_3(\nu_2=1)$ (blue).

distribution peaking at $v'=2$, reflecting the tendency to higher vibrational states as the excitation energy increases.⁵ For $\text{CH}_3(\nu_2=1)$, the SH distribution peaks at $v'=1$, in agreement with the trend described by Parker *et al.* towards a decrease in the vibrational SH excitation with CH_3 umbrella excitation.⁷ For $\text{CH}_3(\nu_1=1)$ a mildly similar anti-correlation is found.

Figure 4 shows the $\text{CH}_3(\nu=0)$ XX sliced image produced in the photodissociation of DMS at 210 nm and the corresponding translational energy distribution. Three differentiated features are observed in the image, namely, a high-recoiled anisotropic ring, an intense and somewhat anisotropic central disk and a rather more diffuse disk with little recoil concentrated in the center of the image. The high-recoiled ring appears in the distribution as a rather narrow, Gaussian-like, peak located at ~ 1.3 eV; the diffuse disk shows as well a Gaussian profile, although partially overlapped with the distribution corresponding to the

central feature. The vertical bars in the Figure represent the available energy E_{av} for the $\text{CH}_3\text{S} + \text{CH}_3(\nu=0)$ channel (at ~ 2 eV) and for the secondary dissociation yielding $\text{CH}_3 + \text{S}(^3P_0)$ by excitation of CH_3S with a probe photon, calculated using Eqs. (1)-(3).

Figure 4: $\text{CH}_3(\nu=0)$ (XX configuration) sliced image obtained from the photodissociation of DMS at 210 nm and the corresponding center-of-mass (CM) translational energy distribution. The vertical bar at ~ 2 eV indicates the available energy for the primary photodissociation process. The combs illustrate a possible vibrational content of the CH_3S co-fragment for modes ν_2 and ν_3 (see the text), while the short bars at the top-left side of the figure denote the available energy for the secondary CH_3S dissociation processes by excitation of CH_3S with a probe photon when considering negligible internal energy for the CH_3S (solid) or the internal energy acquired by CH_3S in the primary dissociation process (dashed).

The envelope of the $\text{CH}_3(\nu=0)$ distribution centered at ~ 2 eV reflects the CH_3S co-product internal (vibrational and rotational energy) distribution convoluted with the CH_3 rotational excitation. The position of the peak, together with the modest full-width-half-maximum (FWHM), suggests an inverted rovibrational distribution population of the fragments, similar to that for the SH product in the photodissociation of CH_3SH . As before, the contribution of internally excited parent molecules seem to be unimportant in the present case. The combs illustrate a possible vibrational energy content for the CH_3S co-fragment.

Based on the calculations of Yarkony,² the ν_3 C-S stretching (727 cm^{-1}) and ν_2 umbrella deformation (1313 cm^{-1}) modes for the CH_3S fragment¹⁵ have been tentatively chosen.

According to the E_{av} bars depicted in Figure 4, the low-recoiled feature is tentatively assigned to the secondary $\text{CH}_3 + \text{S}$ process after one probe photon absorption by the hot CH_3S fragment arising for the primary dissociation. As mentioned above, the position of the short bars at the top-left side of Figure 4 were calculated considering a photon energy of 3.72 eV ($\lambda_{phot} 333.45\text{ nm}$, *i.e.* supposing secondary photodissociation after absorption of a probe laser photon) in Eqs. (1)-(3). The sharp and low-recoiled contribution located at $\sim 0.3\text{ eV}$ (diffuse disk in the image of Figure 4), it is reasonably assigned to dissociative ionization of the CH_3SCH_3 parent.

Photodissociation of CH_3SCH_3 at 201 nm

Figure 5 shows the $\text{CH}_3(\nu=0)$ XX sliced image corresponding to the photodissociation of DMS at 201 nm and the corresponding translational energy distribution. Similarly to the photodissociation at 210 nm , two differentiated features can be observed: a high-recoiled anisotropic ring and a central anisotropic disk.

The features observed in the image are recovered in the distribution. The high-recoiled ring appears as a broad, Gaussian-like, peak located at $\sim 2.2\text{ eV}$ and the low-recoiled contribution presents a Boltmann-like profile. The vertical bar representing the available energy E_{av} for the primary $\text{CH}_3(\nu=0)+\text{CH}_3\text{S}$ channel has been obtained using Eqs. (1) and (3). The bars for the secondary process yielding $\text{CH}_3 + \text{S}(^3P_0)$ by excitation of CH_3S with a probe photon, either with negligible internal energy for the CH_3S (solid line) or with the internal energy arising from the primary dissociation (dashed line), have been calculated using Eqs. (1)-(3).

As in the previous case, the position and width of the TED distribution indicates an inverted rovibrational distribution population of the fragments and negligible contribution from internally excited parent molecules. The combs illustrating vibrational progressions

Figure 5: $\text{CH}_3(\nu=0)$ (XX configuration) sliced image obtained after photodissociation of DMS at 201 nm and the corresponding center-of-mass (CM) translational energy distribution. The vertical bar at ~ 2.2 eV indicates the available energy for the primary process yielding $\text{CH}_3(\nu=0) + \text{CH}_3\text{S}$. The combs illustrate a possible vibrational content of the CH_3S co-fragment for modes ν_2 and ν_3 (see the text), while the short bars at the top-left side of the figure denote the available energy for two possible secondary CH_3S dissociation process by excitation of CH_3S with a probe photon when considering negligible internal energy for the CH_3S (solid) or the internal energy acquired by CH_3S in the primary dissociation process (dashed).

on the ν_3 C-S (727 cm^{-1}) and ν_2 umbrella deformation (1313 cm^{-1}) modes for the CH_3S fragment,¹⁵ are also shown. The low-recoiled feature can be tentatively assigned to the secondary dissociation of the CH_3S fragment at 201 nm, although the width and shape of the contribution cast some doubts about the energy sources and partitioning.

Anisotropy analysis

The stereodynamics of the photodissociation processes studied in this work has been characterized through the speed-dependent Dixon's bipolar moments (BMs).¹⁶

Angular distributions extracted from sliced images are easily fitted to the known expres-

sion for a one-photon dissociation process and $(n+m)$ REMPI detection:¹⁷⁻²⁰

$$I(\theta) = \frac{\sigma}{4\pi} \sum_{i=0}^{2n+2} \beta_i P_i(\cos \theta) \quad (4)$$

where θ is the angle between the photofragment recoil direction and the photolysis laser polarization direction, σ is the absorption cross section, β_i are anisotropy parameters which reflect the dissociation dynamics and the photofragment polarization, P_i are the Legendre polynomials of i -th order and n is the number of photons of the resonant step of the REMPI process.

The XX images comprise alone all the information regarding the dissociation anisotropy and the orientation and/or alignment of the products. In the XZ images, the probe polarization vector lies perpendicular to the detection plane and, therefore, all the information related to the products angular momenta is lost. Similarly, the ZX images have lost the information related to the anisotropy of the dissociation process. The ZZ images do not contain any dynamical information and are used as a reference to avoid systematic errors, such as detector inhomogeneities. Thus, non-zero β_i^{ZZ} parameters extracted from the fit of the ZZ images to Eq. (4) are taken as the instrumental function.

Following the methodology originally described by Grub *et al.*^{21,22} and further developments by Rodríguez *et al.*,^{23,24} the BMs have been calculated from the phenomenological anisotropy parameters extracted out of the CH_3 fragment sliced images. Four bipolar moments have been determined: $\beta_0^2(20)$, $\beta_0^0(22)$, $\beta_0^2(02)$, and $\beta_0^2(22)$, which account, respectively, for the μ - v , v - J , μ - J and μ - J - v correlations, where μ is the transition dipole moment, v the fragment recoil direction, and J the total angular momentum of the detected fragment. The interpretation of the four bipolar moments as a function of the CH_3 speed distribution provides information about the excited-state symmetry, couplings, and dissociation time scales and details about forces and torques between the separating fragments.

For continuous speed distributions, like those measured in this work, a possible partial slicing would have the effect of overlapping signals from different fragment velocities, dis-

torting the photofragment speed and angular distributions. As a standard procedure, we carry out a systematic study of the possible effect of partial slicing in our results through the comparison of the speed distributions obtained with different gate widths, and with pure unsliced images with Abel-inverted VMI distributions.²³ As expected, the differences become inappreciable for a 10 ns gate, as employed in this work.

Figure 6 shows a series of sliced images corresponding to $\text{CH}_3(\nu_2=1)$ fragments produced in the photodissociation of CH_3SH at 210 nm. Similar images have been measured for the $\text{CH}_3(\nu=0)$ and $\text{CH}_3(\nu_1=1)$ fragments (not shown).

Figure 6: $\text{CH}_3(\nu_2=1)$ sliced images obtained after photodissociation of CH_3SH at 210 nm at the four polarization configurations used in this work. The pump and probe laser polarizations are shown on the right side of the images with a double headed arrow (perpendicular to the molecular beam) or a circle and a dot (parallel to the molecular beam). Similar images have been measured for the $\text{CH}_3(\nu=0)$ and $\text{CH}_3(\nu_1=1)$ fragments (not shown).

The speed-dependent BMs obtained from images shown in Figure 6 are plotted in Figure 7. All four BMs take rather constant values throughout the range of velocities spanned for the three vibrational states of the methyl fragment probed, ruling out any vibrational

dependence on the stereodynamics. The $\beta_0^2(20)$ moment, which reflects the μ - v correlation or dissociation anisotropy ($\beta = 2\beta_0^2(20)$) takes rather constant values of $\beta_0^2(20) \sim -0.4$ in rather good agreement with the reported values of β .⁵⁻⁷ The $\beta_0^0(22)$, $\beta_0^2(02)$ and $\beta_0^2(22)$ moments take as well constant values through all the range of CH_3 velocities in the three cases and only a mild dependence on the methyl vibrational state is found. In general terms, the $\beta_0^0(22)$ moment, which accounts for the v - J correlation shows a small, constant value of < 0.1 ; $\beta_0^2(02)$, which accounts for the μ - J correlation takes an averaged value of ~ -0.1 . The triple vector correlation, given by $\beta_0^2(22)$ is coherent with the other two, averaging values close to zero.

Weak vector correlations, reflected in bipolar moments far from the limiting values, are usually associated to vibrational and rotational activity of the parent molecule, which provides both out-of-plane and in-plane motions. Dissociation through a purely repulsive state is faster than the parent molecule rotational period and any photofragment polarization effect that might be observed after photodissociation in a repulsive state must be caused by the initial geometry of the excited photodissociating parent molecule. On the other hand, thermal motion in the electronic ground state of the parent molecule might lead to a breakdown of the so-called unique recoil direction (URD) approximation, which is an extension of the ARL.^{25,26} According to the results shown in Fig. 7, photodissociation of CH_3SH is characterized by a rather strong μ - v correlation, which indicates that the transition dipole moment remains perpendicular to the dissociation plane. The weak v - J and μ - J correlations (given by $\beta_0^0(22)$ and $\beta_0^2(02)$, respectively) indicate, in addition, a scrambled CH_3 rotational angular momentum distribution. The combination of both effects suggests a preferential contribution to the absorption process of in-plane in detriment of out-of-plane vibrational modes.²⁷ Small BM values, on the other hand, could be related to depolarization effects caused by parent rotation during the dissociation process.²⁴

Figures 8 and 9 shows the XX , XZ , ZX and ZZ sets of sliced images corresponding to $\text{CH}_3(\nu=0)$ fragments produced in the photodissociation of DMS at 210 nm and 201 nm,

Figure 7: Speed-dependent Dixon's bipolar moments (BM) obtained from the analysis of the $\text{CH}_3(\nu=0)$, $\text{CH}_3(\nu_1=1)$ and $\text{CH}_3(\nu_2=1)$ images at the four polarization geometries employed in this work (in Figure 6 only the $\text{CH}_3(\nu_2=1)$ images are shown for brevity). The left axis corresponds to the intensity profile, while the BMs are quantified in the right axis.

respectively, and the corresponding bipolar moments are plotted in Figures 10 and 11. Taking into account that the three contributions are not entirely resolved and the BM are equally averaged over the different energy contributions, the results shown in Figures 10 and 11 are strikingly similar to the results obtained for CH_3SH (see Figure 7). The $\beta_0^2(20)$ moment reflects the anisotropy of the main dissociation channel and states, primarily, the dependence of the excitation transitions on the pump laser polarization. The values obtained for $\beta_0^2(20)$ of ~ -0.4 and ~ -0.45 at 210 nm and 201 nm, respectively, and the similitude with the CH_3SH case will be discussed later on the basis of the role of the H-atom (in CH_3SH) and

CH₃ fragment (in DMS) moieties in the dissociation process. Either way, the quasi-limiting values of $\beta \simeq -0.8$ at 210 nm and $\simeq -0.9$ at 201 nm are in excellent agreement with the values reported in the literature.⁸

Figure 8: CH₃($\nu=0$) sliced images obtained after photodissociation of DMS at 210 nm at the four polarization configurations used in this work. The pump and probe laser polarizations are shown on the right side of the images with a double headed arrow (perpendicular to the molecular beam) or a circle and a dot (parallel to the molecular beam).

The $\beta_0^0(22)$, $\beta_0^2(02)$ and $\beta_0^2(22)$ moments obtained for DMS at 201 nm mimic those obtained for CH₃SH (at 210 nm). At 210 nm, the only – and significative – difference found is related to the μ - J correlation, whose associated BM, $\beta_0^2(02)$, takes values ~ 0 (rather than negative) and it could show a lesser vibrational dependence. The positive $\beta_0^0(22)$ values obtained in all cases indicate product rotation (J) parallel to the recoil velocity (v). The

Figure 9: $\text{CH}_3(\nu=0)$ sliced images obtained after photodissociation of DMS at 201 nm at the four polarization configurations used in this work. The pump and probe laser polarizations are shown on the right side of the images with a double headed arrow (perpendicular to the molecular beam) or a circle and a dot (parallel to the molecular beam).

obtained values suggest that the CH_3 fragment shows a timid tendency to spin around the C_3 axis, which is parallel to the recoil velocity, in agreement with the results obtained for the photodissociation of CD_3SCD_3 .⁹ At 201 nm, a small μ - J negative correlation is observed, but it is zero at 210 nm. Such values are consistent with the increase of dissociation anisotropy observed at 201 nm.

Figure 10: $\text{CH}_3(\nu=0)$ speed-dependent bipolar moments (BM) obtained from the analysis of images shown in Figure 8 for the photodissociation of DMS at 210 nm. The left axis corresponds to the intensity profile, while the BM are quantified in the right axis.

Discussion

Photodissociation of CH_3SH *vs.* CH_3SCH_3

If there is anything that should catch the attention of the reader is the strongly similar patterns of the CH_3 translational energy distributions obtained for CH_3SH and DMS, presented in Figures 2 and 4. Both distributions show three components, namely the MPI contribution and the features corresponding to the primary and secondary C-S dissociation channels. The branching ratios between the later two, albeit mode-dependent, do not differ significantly for the vibrationless methyl fragments. The different intensities of the MPI

Figure 11: $\text{CH}_3(\nu=0)$ speed-dependent bipolar moments (BM) obtained from the analysis of images shown in Figure 9 for the photodissociation of DMS at 201 nm. The left axis corresponds to the intensity profile, while the BM are quantified in the right axis.

signal are most probably associated to the different CH_3SH and DMS ionization potentials. Even more noticeable is the fact that the widths of the primary and secondary distributions – which inform about the internal energy of the corresponding co-product – are almost identical for both systems. In other words, the SCH_3 and SH moieties show rather similar internal excitation. Although the CH_3S vibrational distribution does not show up clearly in the CH_3 fragment TED for DMS – while it is plainly visible for CH_3SH in Figure 2 – the anisotropic profile of Figure 4 allows us to guess some structure; furthermore, the presumed structure points towards an inverted vibrational distribution, as for the case of SH . In any case, the narrow distribution and the fact that some structure can be guessed points towards

a modest participation of the vibrational modes of the parent molecule in the dissociation process.

The similarities between the results for CH₃SH and DMS extend to the BMs. The $\beta_0^2(20)$ moment reflects in both cases the nature of the transition involved. The transition moment for the $2^1A'' \leftarrow \tilde{X}^1A_1$ transition is directed perpendicular to the plane containing the C¹-S-C² or C-S-H framework and, therefore, the axial recoil limiting anisotropy parameter for excitation in the first absorption band is $\beta \sim -1$. The fact that in both systems the same β values are obtained indicated that the C²H₃ moiety – the CH₃ forming part of the SCH₃ coproduct – does not break the unique recoil direction approximation.²⁷ According to the previous discussion, the methyl C²H₃ moiety could be tentatively conceived as mere spectator of the process. According to Yarkony,² however, distortion of the S-C²-H angle is decisive for the $C_{2v} \rightarrow C_s$ transition of symmetry that enables the same absorption process. Besides, the CH₃ distribution in Figure 4 for the main channel reflects a vibrational distribution of a low-energetic mode that could possible be assigned to the CH₃S umbrella.

Photodissociation of CH₃SCH₃ at 210 and 201 nm

Despite the apparent differences between the images shown in Figures 8 and 11, when compared the translational energy distributions, the dissimilarities themselves shed light on the reasons behind those differences and on the common mechanism behind. First of all, two features are observed for the photodissociation of DMS at 201 nm, against the three features registered for the process at 210 nm. The distributions are, on the other hand, sensibly wider in the first case. Taking as reference the available energy values for the primary and secondary processes and the CH₃S vibrational progressions, the 201 nm distribution could be viewed as a broadened version of that taken at 210 nm. Such interpretation implies that the low-recoiled contribution in the 201 nm distribution is actually the convolution of other two. A detailed inspection of Figure 11 verifies the former assumption, revealing that the low-energy feature is, actually the convolution of a threshold Boltzmann distribution peaking

at ~ 0.07 eV with a shoulder at ~ 0.19 eV. The two distributions become three, presumably the same observed at 210 nm.

The differences between the results at both photodissociation wavelengths are reduced to the energy partitioning into the fragments and the branching ratio of the different processes. According to Eq. (1), the available energy for the main dissociation channel at 210 nm is 2.01 eV. Since the $\text{CH}_3(\nu=0)$ translational energy distribution peak at $E_T \sim 1.34$ eV, the average fraction of the available energy transferred into the translational energy of the fragments is $\langle E_T/E_{av} \rangle \sim 0.67$. A similar estimation made for the process at 201 nm provides values of 2.2 eV for E_{av} and ~ 1.63 eV for E_T , resulting in an average of $\langle E_T/E_{av} \rangle \sim 0.74$. This result, although in agreement with the values obtained in the literature for the photodissociation of DMS in a wide interval of photolysis wavelengths,^{8,10,28} apparently do not match with the trend found. In an earlier set of experiments carried out by Aoiz and co-workers between 215 and 231 nm,⁸⁻¹⁰ the fraction of the available energy transferred into translational motion was found to decrease with the excitation energy. The average fraction of the available energy transferred into the translational energy of the fragments is calculated from the translational energy at the maximum of the distribution. The $\langle E_T/E_{av} \rangle$ fraction informs, therefore, of the shift produced in the distribution as the available energy increases, but ignores any change produced in the distribution width. The main difference observed between Figures 4 and 5 is precisely the width of the distribution. The increase of the available energy produces a broadening of the main contribution which denotes an increase of the vibrational quanta and/or the number of vibrational states populated in the CH_3S co-fragment. In both cases, the available energy provided by the photon is increasingly transferred into internal energy of the fragments, as reported in the literature.

Promoting modes and spectator modes *vs.* intramolecular vibrational energy redistribution (IVR)

The interplay between similarities and differences between the photodissociation of CH_3SH and CH_3SCH_3 sheds light on the role of certain modes — promotor and spectator — in the photodissociation process of these species and of the randomization of the initial parent excitation (IVR). The fact that some of the vibrational modes of the parent molecule act as merely spectators while others, known as promoting modes, are selectively excited and preserved during the non-adiabatic crossings, indicates that statistical internal redistribution of the vibrational energy (IVR) should not play any major role in the photodissociation process. The similarities between the results obtained for both molecules, namely, the structure of the translational energy distributions, both in components as in branching ratios, and FWHM, and the values of the four BMs extracted, suggest a minor role of the CH_3 moiety in the dissociation process. In this vein, a negligible role of IVR should be assumed. The last statement does not imply, however, that there is not an effective vibrational transfer of energy in the dissociation process or that modes other than the one corresponding to the reaction coordinate are involved. The differences in the seam of conical intersections themselves prove otherwise.

In the photodissociation of methyl mercaptan, the S-H and C-S coordinates are strongly coupled. If the C^2H_3 moiety in the DMS were a mere spectator (quasi-atom) similar coupling should be found for DMS. Instead, the CSC bending and, more interesting, the CH_3 umbrella is known to play a decisive role in the absorption step, which enables the absorption itself and, specifically, the degrading from C_{2v} to C_s symmetries. Furthermore, some vibrational activity is found to endure through the non-adiabatic transition. The CSC bending and the CH_3 umbrella modes act, therefore, as promoting modes which enable the absorption step and, despite the non-adiabaticity of the process, are strongly adiabatically preserved. The information offered by the BMs, although not dramatic in this case, is highly significative. The close to zero values are coherent with minimal distortions of the C-S-C plane and,

surprisingly, the distortions created by the umbrella activity do not show up in the BMs.

Conclusions

The photodissociation of CH_3SH and CH_3SCH_3 from the second absorption band at 210 nm has been studied through the detection of $\text{CH}_3(\nu)$ fragment products using slice imaging. The main dissociation channel in both systems manifests as a highly anisotropic ring. Two additional features, associated to secondary dissociation and multiphoton dissociative ionization processes are observed as well. The corresponding translational energy distributions show inverted vibrational distributions for the respective co-fragments, particularly well resolved for the case of the SH. Speed-dependent Dixon's bipolar moments are extracted yielding anisotropy parameters close to the limiting values, indicating a fast dissociation process in both cases. The similarities between the results obtained for both systems are analyzed and discussed in terms of the role of promoting and spectator modes *vs.* the randomization of internal energy or IVR. Information regarding the energy partitioning between translational and internal modes of freedom is extracted from additional experiments on CH_3SCH_3 at 201 nm.

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