Indene energetic processing in ice mantles in the interstellar medium

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ABSTRACT

Context. Indene, a small PAH, has been detected in the gas phase in the cold dense cloud TMC-1. Due to the low temperature in the cloud, below indene condensation temperature, its presence in the ice mantles of dust grains is likely.

Aims. The aim of this work is to study the stability of indene against the energetic processing by VUV photons or cosmic rays in the ice mantles of dense molecular clouds.

Methods. Ice layers of pure indene or indene diluted in water ice were grown by vapor deposition on a cold surface held at 10 K, 100 K, or 140 K. The samples were processed with VUV photons (120 - 180 nm) and 5 keV electrons and the destruction of indene was monitored by following the decay of its absorption bands in the infrared (IR) spectrum. Finally, we recorded the mass spectra of the decomposition products sublimated by thermal programmed desorption of the processed samples.

Results. Photolysis and radiolysis cross-sections, along with half-life energy doses for indene in the solid form and diluted in water ice matrices at 10 K were derived. Ketones and alcohols were identified as the main processing products in indene and water-ice mixtures.

Conclusions. Dilution in water ice enhances the destruction rate of indene under energetic processing. The molecule is expected to survive for more than 10⁷ yr in the ice mantles of grains in the interior dense clouds, but it will end up getting destroyed within the next few hundred years by the intense VUV field in the diffuse region at the edges of the cloud.

Key words. molecular data - methods: laboratory: molecular - ISM: molecules - Infrared: ISM - astrochemistry

1. Introduction

Polycyclic aromatic hydrocarbons (PAH), as well as other closely related species, are widely assumed to be the carriers of ubiquitous interstellar (IS) emission features known as aromatic infrared bands (AIBs) (Leger & Puget 1984; Allamandola et al. 1985; Tielens 2008). However, the detection of individual PAHs in the interstellar medium (ISM) has proven a major challenge. It is only recently that an individual PAH molecule, namely, in- dene, has been identified in the ISM. This bicyclic molecule, consisting of a six-membered and a five-membered ring, has been found almost simultaneously in the course of the QUI- JOTE (Cernicharo, J. et al. 2021a) and GOTHAM (Burkhardt et al. 2021) surveys of the cold dense cloud TMC-1. An abundance of 1 - 1.6 × 10⁻⁶ relative to H₂ was derived for indene in these observations. This means that indene is exceptionally abundant for its large size, only a factor of five less abundant than the ubiquitous cyclic hydrocarbon c-C₆H₆. Other small related species like benzyne (Cernicharo, J. et al. 2021b) and cyclopentadiene (Cernicharo, J. et al. 2021a,c), as well as the cyano derivatives of benzene (C₆H₅CN), indene (C₅H₄CN), and naphtalene (C₁₀H₈CN) were also found in TMC-1 (McGuire et al. 2018, 2021).

The formation pathway of indene is still a mystery. Gas-phase routes that could be relevant for in situ formation in TMC-1 have been proposed. Doddipatla et al. (2021) suggested that indene can be formed in the gas phase through the barrier-less reaction between the CH radical and styrene (c-C₆H₄C₂H₃), but the presence of a significant quantity of the styrene precursor is dubious in cold and dense environments. McCabe et al. (2020) reported the formation of indene via the reaction of the resonance stabilized allyl radical with o-benzene. The possible generation of aromatic species from simple precursors in the ice mantles of dust grains has also been proposed by Applanalp et al. (2019) based on their experimental results on the processing of acetylene ices with high energy electrons. However, current chemical models of TMC-1 including gas-phase and gas-grain reactions yield too low concentrations of indene as compared with observations (Doddipatla et al. 2021; Burkhardt et al. 2021). Ex situ formation and transfer of PAHs to TMC-1 is also a possibility, but it is unlikely for indene and other small PAHs that will be destroyed by the strong UV galactic field during the evolution of the diffuse to the dense stages of the clouds. Gas-phase models lack a significant number of ion-neutral and radical-radical reactions that could participate in the formation and growth of cycles in cold environments (Cernicharo, J. et al. 2022). Recently, it has been proven that the cyanide derivative of benzene coexists spatially with cyanopolyynes (HC₉N₁₁) and other hydrocarbons, which gives strong support to the formation of these aromatics in situ through gas phase or ice grain processes (Cernicharo et al. 2023). Ion-neutral reactions have been also proposed to explain the formation of cyclopentadiene from C₅H₄ and I-C₅H₅⁺, which leads to the formation of C₅H₇⁺ and of C₅H₈ through dissociative recombination of the cation (Cernicharo, J. et al. 2022).
It is generally assumed that polyaromatic compounds are mostly formed in the outflows of carbon-rich asymptotic giant branch (AGB) stars (Frenklach & Feigelson 1989; Cherchneff, I. 2012) or, more likely, at later stages of stellar evolution like protoplanetary and planetary nebulae (Kwok 2004) through UV processing of the amorphous carbon nanograins and C/H clusters originally formed in the stellar envelopes (Martínez et al. 2020; Santoro et al. 2020), but only large PAHs, with more than \( \approx 50 \) carbon atoms, are expected to withstand the intense UV fields in the transition from the ejecta of evolved star environments to the interstellar medium and later to prestellar cores (Tielens 2008).

At low temperatures (\( \approx 10 \) K) estimated for TMC-1, indene – and complex organic molecules (COMs) overall – are expected to freeze readily on dust grains. Nonthermal desorption mechanisms have been proposed and are being currently investigated to account for their presence in the gas phase. These mechanisms include electron promoted desorption (Marchionne & McCoustra 2016), X ray induced desorption (Torres-Díaz et al. 2023; Kalvàns 2021), desorption induced by exothermic reactions (Garrod et al. 2007; Vasyunin & Herbst 2013) and, notably, UV photodesorption Öberg et al. (2009); Cruz-Díaz et al. (2017) and cosmic ray (CR) sputtering (Dartois et al. 2017, 2022; Pino et al. 2019). Overall, COMs are expected to be highly diluted in the ice mantles of dust grains and on many occasions their gas-phase concentrations should thus be given by the desorption rate of the dominant ice molecules. A recent model estimation by Dartois et al. (2022), assuming pure water ice as well as CR sputtering as the prevailing desorption mechanism, suggests that for the typical conditions of a dense cloud like TMC-1 the gas-to-solid fraction of a typical small aromatic hydrocarbon (they used naphthalene in their calculations) would be just \( \approx 10^{-3} - 10^{-4} \).

In the case of TMC-1, which is a comparatively young object of 0.5-1 Myr (Navarro-Almaida et al. 2021; Chen et al. 2022; Cernicharo, J. et al. 2022), the depletion of hypothetical indene formed in the gas phase might not be so high, but it is still expected to be significant. The stability and chemistry of indene in ice mantles can thus be crucial to understand the global behavior of indene in TMC-1 and this is the subject of the present work. Moreover, the detection of ice-processed indene molecules released to the gas-phase could provide excellent insights into our understanding of the chemistry of small PAHs in these environments.

A large number of studies of PAH photo-processing on ices (usually with UV photons generated by H2 lamps), mostly devoted to photochemistry, have been performed over the last two decades (Bernstein et al. 1999; Bouwman et al. 2011; Cuyllle et al. 2014; Cook et al. 2015; Noble, J. A. et al. 2017; de Barros et al. 2017; Radhakrishnan et al. 2018). In the work by Bernstein et al. (1999) it was observed that the photo processing of PAHs of sizes between those of naphthalene (C10H8) and coronene (C22H22) diluted in water ice leads to the formation of alcohols, quinones, and ethers. The non-volatile products were identified via microprobe laser desorption laser ionization mass spectrometry. Other works have employed mid-IR (MIR) or UV-VIS absorption spectroscopy to analyse the products formed after the VUV-photolysis of PAHs in water ice (Bouwman et al. 2011; Cuyllle et al. 2014; Cook et al. 2015; Noble, J. A. et al. 2017; Noble et al. 2020; de Barros et al. 2017; Radhakrishnan et al. 2018). Compared with the available spectra of PAH cations in argon matrices, it has been observed that photochemical reaction products result from direct photoionization of the PAHs. More recently, experiments have been performed that compare the different products produced by photolysis or radioisolation of PAHs (Cruz-Díaz et al. 2017). However, no information has been given in the previously mentioned works about PAH destruction kinetics.

On the other hand, the radiolysis via keV electron or high-energy ions of PAHs on ices has not received so much attention. In the study by Barnett et al. (2012) ices containing pyrene were bombarded with electrons of energies below 2 keV and the damage of the PAH was used to estimate the penetration depths of the electrons. Again, however, no information about destruction kinetics or destruction products was given.

In the previous paper published by our group (Maté et al. 2023) we reported the IR spectroscopy of amorphous and crystalline indene in a study supported by DFT calculations. In this second part, we address the stability of solid phases of indene at low temperature. Pure indene and its mixtures with amorphous solid water (ASW) at 10 K have been processed with VUV photons and 5 keV electrons, to mimic the effect of the secondary interstellar UV field present in dense clouds, and of cosmic rays, respectively. Moreover, a 130 K pure polycrystalline indene layer has also been energetically processed to simulate its behaviour in warmer astrophysical environments. From the IR spectra and thermal programmed desorption experiments of the processed samples, some reaction products have been identified, offering insights into the solid phase low temperature dissociation chemistry of this species. Also, estimates of VUV and CR destruction cross-sections of indene (pure and in ASW) are given. These data can help in the interpretation of recent indene observations and guide elucidations about its possible formation mechanisms.

### 2. Experimental setup

The experiments were performed in a high vacuum (HV) setup described previously (Maté et al. 2021; Timón et al. 2021), with a background pressure in the \( 10^{-10} \) mbar range. The chamber is provided with a closed-cycle He cryostat and coupled to a FTIR spectrometer through KBr windows. Solid indene layers were grown by vapor deposition on a cold infrared transparent Si substrate placed in thermal contact with the cold head of the cryostat. Indene is a commercial liquid (Sigma Aldrich, \( \geq 99 \% \)) with 1 mbar vapor pressure at 20°C. To grow low temperature solid indene layers, the liquid was placed in a Pyrex tube and its vapor introduced into the vacuum chamber through a needle valve. An independent water line, also provided with a needle valve, was employed to generate indene:water ice mixtures. In order to control the stoichiometry of the mixtures it was experimentally convenient to increase the indene vapor pressure; for that purpose, the Pyrex tube was immersed in a silicone oil bath at 60°C and the line heated. Pure ices were grown at 10 K and at 130 K, while ice mixtures were grown only at 10 K. Typical deposition pressures varied between \( 4 \times 10^{-6} \) mbar for pure deposits and \( 4 \times 10^{-5} \) mbar in the case of the mixtures, and typical deposition times were 5 -30 min. In the high-vacuum chamber, the port for the gas lines is located in a plane about 15 cm below the cold head of the cryostat, between the cold head and the pumping system. This configuration guarantees the backfilling of the chamber with a homogeneous gas pressure and to grow ice layers of equal thickness at each side of the substrate. The deposited indene ice samples and their evolution with processing time were monitored with IR spectroscopy. Normal incidence transmission spectra, with 4 cm\(^{-1}\) resolution and 100 scans accumulation were recorded with a Vertex 70 FTIR spectrometer provided with a MCT detector. A quadrupole mass spectrometer (QMS) (Hiden200) directly connected to the HV chamber.
allows for the gas phase composition in the chamber to be monitored during the experiments.

UV irradiation of the ice layers was carried out with a Hamamatsu L10706 D2 lamp (Maté et al. 2018) that provides a photon flux on the sample, estimated from the data given by the manufacturer, of $\phi_0 = 7.5 \times 10^{11}$ photons cm$^{-2}$ s$^{-1}$. Its emission has a maximum at 165 nm and is largely concentrated in the 120-180 nm range. Electron irradiation was performed with the electron gun described in previous works (Maté et al. 2016). The electron energy was fixed at 5 keV and the flux at $\phi_e = 4 \times 10^{12}$ electrons cm$^{-2}$ s$^{-1}$.

As in our previous works, the processing methodology applied here is to alternatively rotate the cryostat under vacuum to face the ice sample to the VUV (or electrons) beam or the IR beam. In one position, the sample is processed a controlled amount of time and in the other, the IR spectrum is taken in a normal transmission configuration. First, the ice on one side of the Si substrate is processed in this way and then the other. We performed a total of 50 min processing of each side, recoding spectra at time intervals that vary between 1 and 20 min. The evolution of the IR spectra versus processing time shows the decay of the indene features and the growth of new ones.

After energetic processing, we carried out thermal programmed desorption (TPD) experiments of the ice layers. Ramps of 1 K/min from 10 K to 300 K were used, while repetitively recording in the Scan Profile mode of the QMS, scans from 1 to 200 amu at a rate of 1 scan 68 s.

### 3. Results

#### 3.1. Deposited samples

Amorphous and polycrystalline indene solid layers, grown by vapor deposition at 10 K and 130 K, respectively, and 10 K indene:water ice mixtures, with a very small number molecule fraction of indene (between 1 and 3 %) were studied. The fresh deposited samples were characterized by their IR absorbance spectra. Typical spectra of amorphous and crystalline indene solids are shown in Maté et al. (2023). Spectral assignments and band strengths of the absorption features in the 4000-500 cm$^{-1}$ interval are also given in Maté et al. (2023). Examples of the IR spectra of the ices grown in this work are shown as black traces in Figures 1 and 2. Providing the IR band strength (A) is known, the column densities of the deposited indene samples can be estimated. We have taken in all cases the band at 768 cm$^{-1}$ (out-of-plane in-phase CH bending) with A of $2.0 \times 10^{-17}$ cm/molec and $2.3 \times 10^{-17}$ cm/molec for amorphous and crystalline samples, respectively. This band is the most intense absorption feature in the indene spectra and although it overlaps with the libration mode of water at aprox. 800 cm$^{-1}$, its smaller FWHM allows for a proper separation of the indene absorption contribution. The column densities of amorphous solid water (ASW) in the indene-water ice mixtures were calculated from the $v$ OH band taken a band strength of $2 \times 10^{-16}$ cm/molec for ASW at 10 K (Mastrapa et al. 2009). Possible modifications of indene or water band strengths in the indene:water mixtures have not been considered. The column densities of indene and water estimated in this way for the samples used in the processing experiments are listed in Table 1.

<table>
<thead>
<tr>
<th>List of experiments</th>
<th>Sample</th>
<th>T(K)</th>
<th>N$_{indene}$ molec cm$^{-2}$</th>
<th>N$_{water}$ molec cm$^{-2}$</th>
<th>$\rho$ g cm$^{-3}$</th>
<th>h each face nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>VUV1: indene, amorphous</td>
<td>10</td>
<td>1.2</td>
<td>1.3</td>
<td>24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VUV2: indene, crystalline</td>
<td>130</td>
<td>3.0</td>
<td>1.4</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VUV3: indene (3%/water)</td>
<td>10</td>
<td>2.4</td>
<td>8.2</td>
<td>0.67</td>
<td>210</td>
<td></td>
</tr>
<tr>
<td>VUV4: indene (1%/water)</td>
<td>10</td>
<td>1.1</td>
<td>12</td>
<td>0.66</td>
<td>290</td>
<td></td>
</tr>
<tr>
<td>ELE1: indene, amorphous</td>
<td>10</td>
<td>1.3</td>
<td>1.3</td>
<td>95</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ELE2: indene, amorphous</td>
<td>10</td>
<td>8.6</td>
<td>1.3</td>
<td>62</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ELE3: Indene, crystalline</td>
<td>130</td>
<td>2.1</td>
<td>1.4</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ELE4: indene (1.5%/water)</td>
<td>10</td>
<td>2.6</td>
<td>17</td>
<td>0.66</td>
<td>400</td>
<td></td>
</tr>
</tbody>
</table>

#### 3.2. Products of energetic processing

##### 3.2.1. Infrared spectra

Looking at the IR spectra of the processed samples, it is possible to extract some information about the species that form after the destruction of indene. Figure 1 shows photolysis experiments and Figure 2 radioysis experiments. The spectra at the end of the processing time are presented for the pure indene at 10 K, and indene diluted in ASW at 10 K, together with the initial ones. For a clear identification of the new emerging features, and for a better comparison of radioysis versus photolysis chemistry, in Figure 3 we present the difference, final minus initial, spectra of the spectra shown in Figures 1 and 2. The main new features are listed in Table 2. In the discussion below, we provide possible destruction products that could be the carriers of the new IR features. The processing experiments could lead to the ionization of the indene molecule, as observed for larger PAHs. The ionization energy of indene is 8.16 eV (Zhou et al. 2009) in the gas phase. Woon & Park (2004) reported that the ionization energies of PAHs embedded in ice decrease with respect to those of the gas phase (for benzene, naphthalene, anthracene, and pyrene). A decrease in the ionization cross section with increasing cluster size was also observed for larger PAHs than indene (Joblin et al. 2017). Therefore, it is probable that the indene molecule, both in the pure solid form or diluted in water ice, will be easier to ionize than in the gas phase, and that both processing agents (VUV photons or keV electrons) employed in this work will cause some ionization. Unfortunately, the IR spectrum of the indene ion has only been reported theoretically and for the gas phase and therefore it is difficult to establish its presence in the processed ices of this work.

Most of the new peaks in the IR spectra are common to photolytically generated species linked to a phenyl group, suggesting the formation of species like tolucene or styrene, after the breaking of the five-member ring of indene (Pitzer & Scott 1943; Wilmshurst & Bernstein 1957).

A broad new absorption appears around $\approx 1660$ cm$^{-1}$ that is stronger in the samples containing water. For the pure indene...
Table 2. New absorption peaks observed in the processed ices at 10 K and tentative assignment to molecular group vibrations.

<table>
<thead>
<tr>
<th>Pure ELE</th>
<th>pure VUV</th>
<th>1% in H$_2$O, ELE</th>
<th>1% in H$_2$O, VUV</th>
</tr>
</thead>
<tbody>
<tr>
<td>2953, 2936</td>
<td>2936, 2936</td>
<td>2977, 2940</td>
<td>2970, 2940</td>
</tr>
<tr>
<td>2867, 2844</td>
<td>2857, 2844</td>
<td>2870, 2840</td>
<td>2870, 2850</td>
</tr>
<tr>
<td>2337</td>
<td>2337</td>
<td>2343</td>
<td>2343</td>
</tr>
</tbody>
</table>

υ$_{\text{CH}_1, \text{CH}_2}$, toluene, styrene

| 2266 - 2258 | 2277, 2244 | 2277 |
| 2138 (sh) | - | - |

υ$_{\text{CO}_2}$

| 2133 | 2132 | 2138 | 2138 | 2108 |
| 2108 | 2114 (w) | 2108 |
| - | 1850 | - | - |

υ$_{\text{CN, OCN}}$

| 1716 - 1598 | 1724 (broad) | 1750 (w, narrow) | 1680 (broad) |
| 1478 | 1478 | 1478 |
| 1438 | 1437 |
| 1154 |

υ$_{\text{C=C}}$ styrene, toluene

| 1270, 1248 | - | - | - | - |
| 753 | 753 |
| - | - | - |
| - | 650 | 650 |

υ$_{\text{C=O of aryl-ketones}}$

<p>| 1438 |</p>
<table>
<thead>
<tr>
<th>1154</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
</tr>
</tbody>
</table>

υ$_{\text{CO (Aryl) CH-CH}_2\text{OH}}$

| 1750 | 1750-1700 |
| 1700 |
| 1680 |
| 1650 |

υ$_{\text{CH}}$ of di-substituted benzenes

| 1478 |
| 1461 |
| 1036 |
| 650 |

υ$_{\text{CH}}$ of new formed species

**Fig. 1.** MIR spectra of indene ices before (black traces) and after (red traces) UV irradiation (50 min each face). Spectra of the processed ices (red traces) have been displaced in the vertical axis for better visualization. Top and bottom panels correspond to the VUV1 and VUV3 samples listed in Table 1.

**Fig. 2.** MIR spectra of indene ices before (black traces) and after (red traces) high energy (5 keV) electron bombardment (50 min each face). Spectra of the processed ices (red traces) have been displaced in the vertical axis for better visualization. Top and bottom panels correspond to the ELE1 and ELE4 samples listed in Table 1.

samples, styrene and toluene C-C stretching can contribute in this region. In particular the C=C stretching of the vinyl group of styrene appears at 1650 cm$^{-1}$ (Hermán et al. 2015). For indene: water samples, the broad strong absorption at 1700-1550 cm$^{-1}$ is most probably due to C=O stretching group vibrations of aromatic ketones. The formation of these species in the photolysis of PAHs diluted in water ice has been stated in previous literature studies (Bernstein et al. 1999; Cook et al. 2015). In the pure indene experiments, oxygen could be also present in small amounts, due to residual H$_2$O contamination in the high vacuum chamber. The CO vibration has a strong band strength as compared to C=C, and even a small fraction of oxygen could give a significant IR absorption.

New bands are observed at 1474 cm$^{-1}$ and at 1438 cm$^{-1}$ as shoulders at the high and low wavenumber wing of the 1458 cm$^{-1}$ in-phase in-plane hexa-ring CH bending indene mode, and at 753 cm$^{-1}$, in the low wavenumber wing of the strong in-plane out-of-plane CH bending of indene at 768 cm$^{-1}$ (an assignment of the main solid indene modes is given in our previous paper (Maté et al. 2023)). The new features are clearly seen in the pure species experiments but not so clearly in the indene:water ones; this is likely due to the fact that the bands get broader in the water ice matrix. It is plausible that the new bands will be associated...
with the same kind of motions but for species that have suffered
some modifications, as in the previously mentioned ketones or
alcohols. The indene cation is also a candidate, its calculated
spectrum is provided in the NASA PAH database (Bauschlicher
et al. 2018) and has a quite strong peak at 770 cm

Other weak features at 1270 cm
, 1248 cm
, 1189 cm
, and
1154 cm
 are observed in the spectrum of pure indene pro-
cessed with electrons and have been listed in Table 2. Their
presence in electron processing and not in VUV processing is
attributed to the smaller amount of indene processed in the later
experiment, not to differences in the chemistry. No clear candi-
date is suggested for these absorptions.

In the low wavenumber region, a new band at 650 cm
 is ob-
served in the experiments with water, however, it is not present
in pure indene experiments. It could be tentatively assigned to
the 6 in-phase-out-of-plane CH bending of some O-containing
benzene derivative (Socrates 2001). This band, together with the
intense and broad band at 1700 -1550 cm
 suggest that a differ-
et chemistry takes place when indene is diluted in a water ice
matrix (compare top and bottom panels in Figure 3). This has
indeed been observed and a quantification to support it is given
below, namely, that indene destruction is much more efficient in
water ices than in pure samples, both by radiolysis or photolysis.

Apart from the new bands associated tentatively to new aromatic
species, in the 2500 cm
 – 2000 cm
 region, we observe a set
of new features which carriers are most likely lighter species as
CO
 (2337 cm
) or CO (2133 cm
). The weak bands that ap-
pear in the 2256 cm
-2277 cm
 range depending on the exper-
iment could be assigned to the CO stretching in N-C-O groups,
where the N atom must come from a nitrogen impurity in the
high vacuum chamber. Finally, an unidentified new absorption is
observed at about 2110 cm
.

An inspection of the data in the bottom panel of Figure 3 hints
at some differences in the chemistry induced either by VUV
photons or by electrons in the indene:water samples. First, a
larger amount of CO
 is formed in the electron radiolysis as
compared with the VUV photolysis. For a given number of de-
stroyed indene molecules, radiolysis yields three times more
CO
 molecules. Some of the C atoms can come from CO
 impurities in the vacuum chamber, but this fraction is almost the
same for both processing agents when no water is present (see
top panel of Figure 3). Therefore, this observation indicates that
in the water ice electron processing experiments a larger fraction of
the indene destruction leads to the formation of CO
 and sug-
gests a higher degree of fragmentation. Second, a band at 1036
 cm
 appears in the photolysis experiment and not in the radiol-
ysis one. Finally, for a similar destruction fraction, the strength
of the 650 cm
 band is larger in the electron processing exper-
iment. A probable candidate for the molecule that can form after the breaking of the penta-ring, maintaining two of the C atoms in an aliphatic
chain where some H and an OH group have been added. The
lack of this alcohol in the electron processing experiment indi-
cates a larger erosion of the indene destruction products, which
leads to the formation of small molecules such as CO
. The car-
rier of the 650 cm
 band must be therefore a more resistant,
most likely aromatic, species.
3.2.2. Thermal programmed desorption

Infrared spectroscopy allows for the detection of functional groups, but unfortunately it is neither very sensitive nor selective enough for the identification of the specific molecular carriers of the observed absorption bands, especially for species of relatively large masses. To obtain complementary information, we have also performed thermal programmed desorption experiments involving the mass spectrometric detection of the desorbed molecules.

Figure 5 displays the TPD mass spectra of indene samples processed with 5 keV electrons. It presents scans recorded after reaching a temperature of 270 K for an 1.5% indene in water mixture (trace a), for pure indene (trace b), and for pure unprocessed indene (trace c) as a reference. This temperature has been selected because at 270 K the products of irradiation, especially those less volatile, reach their maximum signals. In contrast, indene and water have already evaporated to a great extent, as well as lighter products such as H$_2$, CO$_2$, light aliphatic species, and so on, which can also contribute significantly to the background signal. Therefore, the displayed mass range, between 70 and 152 amu, provides the most interesting parts of the three mass spectra, which have been displaced along the vertical axis for the sake of clarity.

![Fig. 5. Mass spectra recorded when a temperature of 270 K has been reached in the TPD processes, of indene processed with 5 keV electrons for pure indene (ELE2) (b) and indene:water (ELE4) (a).](image)

Over the mass range shown, we see that indene has a complex mass spectrum, with plenty of peaks spanning up to 118 u. The highest intensities correspond to the peaks at 115 and 116 u (Figure 5c). When pure indene is processed, traces of some other peaks begin to appear (Figure 5b), which indicate the formation in small proportions of the products of pure indene destruction chemistry, as well as (conceivably) products of the destruction of indene plus background water trapped in the sample during the whole deposition and irradiation process at 10 K. At the same time, indene is lost during irradiation as shown by the appreciable decay of the corresponding peaks in the spectrum.

In the co-deposited water-and-indene sample, (Figure 5a), the formation of new products is clearly seen in the growth of peaks in the mass intervals 75-80 u, 91 u, 100-105 u, 129-134 u, and 145-150 u. The identification of the new products is difficult due to the overlapping of fragment peaks from different species, but the sets of peaks observed are consistent with expected processing products and with the data from IR spectra. Under 5 keV electron bombardment the indene molecules in the ice can be directly destroyed leading to the formation of benzene (with a maximum peak at 78 u), toluene (with a maximum peak at 91 u), and styrene (with a maximum peak at 104 u). Note, that for all these species the more stable six-membered aromatic ring is preserved. Besides the product of direct fragmentation, indene can react with OH and H atoms resulting from the destruction of the water molecules. Reactions with OH will likely give rise to alcohols like indanone, C$_9$H$_{10}$O, (with a maximum peak at 105 u) and ketones such as indanone, C$_9$H$_8$O (with peak maximum at 104 and 132 u). These molecules have isomers that can slightly change the fragmentation pattern within the mentioned sets of peaks. Products of double oxygenation, such as hydroxy-indanone, C$_9$H$_6$O$_2$, are also possible and would be responsible for the smaller set of peaks at 145-150 u.

A study of the evolution of some of the main mass peaks with temperature in the TPD experiments can shed some light about the different volatility of possible processing products. Figure 6 shows results of the TPD experiments for the mixtures of indene and water ices processed, both with electrons (Figure 6a), and with UV photons (Figure 6b). The signals at 115 and 116 u correspond to the highest peaks of indene, which shows a maximum sublimation around 180 K. For the other signals, differ-
ent behaviour can be appreciated among the masses 104 (pink colour in Figure 6), 133-134 (green), and 120-148 u (blue). The three groups sublime with a different profile and reach the sublimation maximum at a different temperature. It seems that the heaviest species sublime later. We note that mass 120 u is likely a fragment of one of the compounds with their maximum mass peaks at 148 amu. This behavior can be observed, both with electrons and with UV processing, although the efficiency of the UV irradiation is noticeably lower.

3.3. Kinetics

Indene destruction under irradiation with VUV photons or high energy electrons will be assumed to follow first-order destruction kinetics, characterized by a destruction cross-section, $\sigma_{\text{des}}$:

$$N(t) = N_0 e^{-\sigma_{\text{des}} F t},$$

where $N$ represents the concentration of indene and $F$ is the fluence, usually expressed in photons or electrons cm$^{-2}$. Since the concentration of indene is proportional to the intensity of its absorption bands in the absorbance spectrum, Eq. (1) can be transformed into:

$$\ln \frac{I_F}{I_0} = -\sigma_{\text{des}} F,$$

where $I_0$ and $I_F$ represent the initial intensity and the intensity at fluence $F$ of a particular indene absorption band. During the irradiation process, the decomposition products might react back to form the precursor or evolve giving secondary species. These effects will lead to a deviation from the linear behavior expressed by Eq. (2). With the aim of extracting a destruction cross-section, we assume that the equation describes the destruction at least at the beginning of energetic processing.

Since the different bands correspond to different molecular vibrations and involve different bonds, it is possible that they evolve differently with time leading to different destruction cross-sections. We have analyzed all the indene bands with a high-enough signal-to-noise ratio (S/N) in the IR spectrum to be able to follow their evolution with processing time. Differences are observed both in the decay speed and in attenuation fraction, mostly in the pure indene experiments. Roughly, they can be grouped in two sets, an example of some of the decays is given in Figure 7.

We decided to extract destruction cross-sections from two of the strongest indene bands, at 1458 cm$^{-1}$ and at 768 cm$^{-1}$, that are representative of the fast and slow destruction tendencies observed. Both bands are assigned to a CH bending modes, but they will be sensitive to modifications of the aromatic structure of the indene molecule and also to H substitutions by other groups. To follow the destruction of one of the indene rings more directly, it would be necessary to monitor the decay of the band assigned to a C=C mode, which appears about 1610 cm$^{-1}$. However, except for the pure indene electron processing experiment, the absolute intensity and the decay of this band is very weak, and we could not extract reliable destruction cross-sections from it.

3.3.1. VUV Photolysis

Ices usually absorb a large fraction of VUV radiation. For that reason, in many cases, the ice samples grown in the laboratory cannot be considered to be optically thin. When that happens, the attenuation of the initial photon flux, $\phi_0$, during the passage of the VUV beam through the ice layer has to be taken into account. An approximation that can be made is to consider an average photon flux, $\phi_{av}$, that will be estimated as (Maté et al. 2021):

$$\phi_{av} = -\frac{\phi_0}{N_0\sigma_a} (e^{-\sigma_a N_0} - 1),$$

where $\sigma_a$ is the ice VUV absorption cross-section. For a binary mixture the absorption cross-section can be roughly approximated by $\sigma_{av} = f_1\sigma_1 + f_2\sigma_2$, where $f_i$ is the molecular fraction and $\sigma_i$ the absorption cross-section of component i. This average flux is employed to estimate the fluence as: $F = \phi_{av} \Delta t$, where $\Delta t$ is the processing time. However, in order to perform these calculations, the VUV absorption cross-section of the ice is needed. The average absorption cross-section of water ice over the 120-180 nm range, $\sigma_{av}$(H$_2$O) $\approx$ 3 x 10$^{-17}$ cm$^2$, was taken from Cruz-Diaz, G. A. et al. (2014). For indene, the experimental literature data available are for the species in solution and show that the absorption grows to lower wavelengths, the maximum being about 3 x 10$^{-17}$ cm$^2$ at 200 nm, the lower wavelength measured (Garratt 1993; Rambart-Lucas 1950). The gas-phase VUV absorption cross-sections measured from benzene, naphthalene, and cyclopentene (Keller-Rudek et al. 2013) have maximum values that vary between 2.6 x 10$^{-17}$ cm$^2$ and 4 x 10$^{-16}$ cm$^2$, located between 180 nm and 200 nm, depending on the species. Calculations for the indene molecule performed by Borin & Serrano-Andrés (1999) found that the UV indene spectrum has two strong absorptions at 5.0 eV (248 nm) and 5.9 eV (210 nm), with the second one being the strongest. Combining the experimental and theoretical information available, it seems reasonable to assume 3 x 10$^{-17}$ - 3 x 10$^{-16}$ cm$^2$ as lower and upper limits for the indene average absorption cross-section over the wavelength range of the D$_2$ VUV lamp. In the present work, these two limiting values are considered to estimate the average flux via Eq. (3), that is then used to estimate $F$ and subsequently derive the indene destruction cross-sections via Eq. (2).

The decay versus processing time of the bands at 1458 cm$^{-1}$ and at 768 cm$^{-1}$ for the four VUV experiments listed in Table 1 are depicted in Figures 7 and 8.
shown in the left panels of Figure 7. Fitting the linear part of the logarithmic representation of those decays versus fluence gives the cross-sections that are listed in Table 3. It can be seen that the linear behavior extends up to 30 min processing for the 130 K experiment. For pure indene at 10 K and indene:water ices the linear behavior is observed only for the first \( \approx 10 \) min of processing, corresponding to fluences up to \( 1 - 2 \times 10^{16} \) ph/cm\(^2\).

From Figure 7 and the cross sections listed in Table 3 it can be seen that indene photolysis is very much enhanced by the water ice environment, with band intensities decaying faster in the water ice mixtures. This large enhancement of the photolysis caused by water ice was not observed for other species investigated in our group. For example, methylisocyanate when diluted at 4\% in water ice shows a moderate decay in the photolysis cross-section as compared with that of the pure species (Maté et al. 2018). In the case of 2-aminooxazole (Maté et al. 2021), no effect of the water ice matrix was observed on the VUV destruction cross-section. Regarding the absolute cross-section values, indene is more labile versus photolysis at 10 K, both pure or mixed with water, than other COMs like urea (Herrero et al. 2022) or methylisocyanate.

In relation with the different decays of the two indene modes chosen, for the pure species the destruction of the molecular groups responsible for the in-phase out-of-plane CH bending (768 cm\(^{-1}\)) is faster than that associated with the in-plane hexagonal CH bending (1458 cm\(^{-1}\)). The differences, if they exist, are smaller in water diluted samples, where the two cross-sections are equal, within the mutual experimental uncertainty (see Table 3). This can be an indication of a different destruction chemistry in the two kinds of ices (pure versus mixed with water).

### 3.3.2. Electron radiolysis

Figure 8 shows the evolution of the bands at 1478 cm\(^{-1}\) and 768 cm\(^{-1}\) of indene for the electron processing experiments listed in Table 1. The linear behavior extends up to 30-40 min, corresponding to fluences of \( 1 \times 10^{16} \) e/cm\(^2\), in the pure species experiments. In contrast, the linear behavior is not clearly seen in the water mixture experiment, where the criterion was to fit the first five minutes of the decay. The destruction cross-sections for electron bombardment are listed in Table 4. In analogy with the VUV photolysis experiments, indene destruction is enhanced by the water ice matrix.

As for the comparison of the decays of the two bands, for pure indene ices the tendency is similar to that observed for VUV processing, the 768 cm\(^{-1}\) mode decays faster than the 1458 cm\(^{-1}\) mode. And for mixtures, again in agreement with VUV experiments, the difference of the destruction cross-sections of the two bands lies within experimental error, that is large in these very diluted samples.

### 3.3.3. Energetic destruction yields.

The energetic cost for the destruction of indene ices with UV photons and 5 keV electrons can be estimated with the cross-sections derived in the previous section. The amount of energy needed to reduce by one half the initial number of indene molecules, known as half-life dose, can be estimated from Eq. (2): The half-life fluence is defined as:

\[
F_{1/2} = \ln 2 / \sigma_{des}.
\]

And the half-life dose is then given by:

\[
D_{1/2} = \frac{F_{1/2} \ f_E \ E}{\ln(2) \ f_E \ E} = \frac{\ln(2) \ f_E \ E}{\sigma_{des} \ N_0},
\]

where \( f_E \) is the fraction of energy deposited by the photons or electrons in the sample, \( E \) is the photon (average, 8.1 eV in this work), or electron energy and \( N_0 \) is the initial column density. In the electron processing experiments, the energy is deposited in an approximately homogeneous way throughout the sample that can be quantified by means of a linear energy transfer, \( LET \), and Eq. (5) is then expressed as:

\[
D_{1/2} = \frac{\ln(2) \ LET}{\sigma_{des} \ \rho},
\]

where \( \rho \) is the volume density. For a binary mixture it can be roughly approximated by \( \rho \approx \rho_1 f_1 + \rho_2 f_2 \), where \( f_i \) is the fraction of the ith component. The linear energy transfer for our experiments were calculated with the CASINO code Drouin et al. (2007). The LET values and are listed in Table 4.

In the photolysis experiments, due to indene absorption, the incident radiation can be significantly attenuated within the sample and, therefore, the absorption of energy is not homogeneous throughout the sample thickness. For this case, the optically thin limit (\( N \to 0 \)) has to be considered (Maté et al. 2021) and within this limit:

\[
D_{1/2} = \ln(2) \frac{E \ \sigma_a}{\sigma_{des}}.
\]

where \( \sigma_a \) is the absorption cross section. Then, for each component in a mixture, the half-life dose is given by (Maté et al. 2021):

\[
D_{1/2}(i) = \frac{\ln(2) \ E \ \sigma_a}{f_i \ \sigma_{des}(i)},
\]

where \( \sigma_a \) is the absorption cross-section of the mixture and \( f_i \) the molecular fraction of component i. The \( D_{1/2} \) obtained for the photolysis and electron radiolysis of the various ices studied in this work are listed in Tables 3 and 4.
In contrast, indene in ice mantles toward the di
2021; Chen et al. 2022; Cernicharo, J. et al. 2022). The derived
a best-fit time in the range 0.5-1 Myr (Navarro-Almaida et al.
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TMC-1 have recently been the subject of thorough studies com-
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one, since it gives the lower limit for bond breaking in indene.

The properties of cold molecular clouds show large variations
between the diffuse and the dense medium (Snow & McCall
2006). With increasing density, the VUV field and, to a lesser
extent, the CR flow become appreciably attenuated. Approxi-
mate values of the energy dose rates imparted by VUV photons
and CRs on the ice mantles of dust grains have been provided
by Moore et al. (2001) for the two extreme cases of diffuse and
dense molecular clouds. We have used these values and the ex-
perimental half-lives of indene in water ice determined in
this work, to estimate the half-life of indene in these two envi-
ronments (see Table 5). Considering the approximations made
in Moore et al. (2001) and the experimental uncertainty of the
present measurements the derived half-lives must be considered
as order of magnitude estimates.

The composition and properties of the prototypical dark cloud
TMC-1 have recently been the subject of thorough studies comb-
ing observations with the discovery of a plethora of new
molecules with the QUIJOTE and GOTHAM line surveys (see
Cernicharo, J. et al. (2021a, 2022, 2023); Cabezas, C. et al.
2023); McGuire et al. (2018, 2021); Remijan et al. (2023) and
references therein) and chemical models (Fuente et al. 2019;
Navarro-Almaida et al. 2021; Chen et al. 2022; Cernicharo, J.
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lifetime for indene in ice mantles (Table 5) is appreciably larger.
In contrast, indene in ice mantles toward the diffuse cloud region

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\phi_{\text{av}}$</th>
<th>LET</th>
<th>$\sigma_{\text{des}}$</th>
<th>$D_{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(10$^{13}$ ph. cm$^{-2}$s$^{-1}$)</td>
<td>keV/µm</td>
<td>(10$^{-17}$ cm$^2$)</td>
<td>eV/molec</td>
</tr>
<tr>
<td>VUV1</td>
<td>4.8 / 0.79</td>
<td>6.8 / 34</td>
<td>15 / 72</td>
<td>25 / 50</td>
</tr>
<tr>
<td>VUV2</td>
<td>5.0 / 0.85</td>
<td>1.3 / 8.0</td>
<td>8.3 / 59</td>
<td>130 / 211</td>
</tr>
<tr>
<td>VUV3</td>
<td>2.2 / 0.75</td>
<td>50 / 90</td>
<td>67 / 96</td>
<td>14 / 25</td>
</tr>
<tr>
<td>VUV4</td>
<td>1.9 / 1.1</td>
<td>34 / 97</td>
<td>49 / 135</td>
<td>54 / 35</td>
</tr>
</tbody>
</table>

Table 4. Destruction cross-section of 5 keV electrons for pure indene and indene-water ice samples. (uncertainties given in %). $\phi_{\text{av}}$, electron flux; $\sigma_{\text{des}}$, destruction cross-section (± 20% for pure species, ± 30% for the mixture, fit to Eq. (2)); $D_{1/2}$, are the half-life doses estimated using Eq. (6).

4. Astrophysical implications

Indene, if indeed present on the surface of ice grains, is expected
to be at most a minor component in ice mixtures dominated by
water and with a significant proportion of CO and CO$_2$. We have
thus taken the half-life doses of the indene-water mixtures for
the calculation of the half-lives of indene in space ices. From
the two half-life doses available, corresponding to the different
decay rates of the CH bending bands, we have chosen the lowest
one, since it gives the lower limit for bond breaking in indene.

The properties of cold molecular clouds show large variations
between the diffuse and the dense medium (Snow & McCall
2006). With increasing density, the VUV field and, to a lesser
extent, the CR flow become appreciably attenuated. Approxi-
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and CRs on the ice mantles of dust grains have been provided
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ronments (see Table 5). Considering the approximations made
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lifetime for indene in ice mantles (Table 5) is appreciably larger.
In contrast, indene in ice mantles toward the diffuse cloud region

| Table 3. VUV destruction cross-sections for pure indene and indene/water ice samples. The two values listed in each column correspond to calculations performed assuming different VUV absorption cross-sections for indene ($\sigma_{\text{indene}}$: 3 × 10$^{-13}$ cm$^{-2}$ or 3 × 10$^{-14}$ cm$^{-2}$); $\sigma_{\text{des}}$, destruction cross-section (± 30% for pure indene, ± 40% for mixtures, fit to Eq. (2)). $D_{1/2}$, are the half life doses estimated using Eqs. (7) or (8). |
|-------------|------------------|-----------------|-----------------|-----------------|
| Sample      | $\phi_{\text{av}}$ | $\sigma_{\text{des}}$ | $D_{1/2}$ |
|             | (10$^{13}$ ph. cm$^{-2}$s$^{-1}$) | (10$^{-17}$ cm$^2$) | eV/molec |
| VUV1        | 4.8 / 0.79       | 6.8 / 34         | 15 / 72        | 25 / 50         |
| VUV2        | 5.0 / 0.85       | 1.3 / 8.0        | 8.3 / 59       | 130 / 211       |
| VUV3        | 2.2 / 0.75       | 50 / 90          | 67 / 96        | 14 / 25         |
| VUV4        | 1.9 / 1.1        | 34 / 97          | 49 / 135       | 54 / 35         |

Some COMs typical of hot cores and coronas such as C$_2$H$_5$CHO,
C$_3$H$_7$OH, HCOOCH$_3$, CH$_3$OCH$_3$, CH$_3$CH$_2$OH, CH$_3$COCH$_3$, CH$_3$CH$_2$CHO, and CH$_3$CHCO have been found in TMC-1
(Agündez, M. et al. 2021, 2023; Fuentetaja, R. et al. 2023) which
suggests a possible release of molecules to the gas phase from
the surface of the grains. However, their abundances in TMC-1
are rather low compared with the carbon-bearing species formed
in the gas-phase.

The release of ice-processed indene products to the gas phase
could be studied through sensitive line surveys such as QUIJOTE
(Cernicharo, J. et al. 2021b). So far, only CCH and CN deriva-
tives of benzene, indene and naphthalene have been observed.
Most of the large cycles produced in the gas phase (Cernicharo,
J. et al. 2023) and detected towards TMC-1 are being incorpo-
rated into the grain surfaces during the chemical and dynami-
elic evolution of the cloud. These species will be well protected
against UV radiation during most of the cloud evolution. Hence,
deposited indene and other small PAHs could survive UV de-
struction, thereby providing time for their reaction with H$_2$O and
to the production of PAH-based COMs. In the future, improved
QUIJOTE data could enable the detection of some O and OH
derivatives of these species (as those found in our experiments),
which will certainly provide additional insights into the chem-
istry of cold dark clouds.

5. Summary and conclusions

Motivated by the recent detection of indene in the gas phase in
cold regions in the ISM and with the aim to help understand the
Table 5. Lifetimes of indene in astrophysical environments. For cold dense clouds the VUV half-life was calculated with half-life doses corresponding to 1% indene in ASW at 10 K. The CR half-life was calculated with the half-life dose of 3 eV/molecule for 1% indene in ASW at 10 K.

<table>
<thead>
<tr>
<th>Environment</th>
<th>VUV dose rate (eV/molecule/yr)</th>
<th>CR dose rate (eV/molecule/yr)</th>
<th>VUV half-life (yr)</th>
<th>CR half-life (yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cold dense cloud (T&lt;30K)</td>
<td>4 × 10⁻⁷</td>
<td>3 × 10⁻⁷</td>
<td>0.7–1 × 10⁸</td>
<td>1 × 10⁸</td>
</tr>
<tr>
<td>Cold diffuse ISM (T=30-100 K)</td>
<td>0.1</td>
<td>3 x 10⁻⁶</td>
<td>2.7–4.1 × 10⁻²</td>
<td>1 × 10⁶</td>
</tr>
</tbody>
</table>

a) (Moore et al. 2001). In this reference, UV doses are estimated for typical ice mantles with a thickness of 20 nm.