IR spectroscopy and energetic processing of methyl isocyanate ice

V. J. Herrero, B. Maté, G. Molpeceres, V. Timón, I. Tanarro, R. Escribano* and R.J. Peláez
Instituto de Estructura de la Materia, (IEM-CSIC), Madrid, Spain,
(*) *rafael.escribano@csic.es*

Introduction

Methyl isocyanate has been recently detected in the interstellar medium [1-2], whereas a reported detection on comet 67P/ Churyumov-Gerasimenko (67P/C-G) could not be confirmed [3]. Although this molecule was usually neglected in astrochemical networks, this new evidence fosters new astrophysical studies on this species to be carried out. We present here our work on the IR spectra and on the energetic processing of ices of this molecule.

Crystalline structure and IR spectroscopy

No X-ray structure has been reported for crystalline CH_3NCO. We have derived a tentative structure by taking as a starting point the crystal of isocyanic acid.

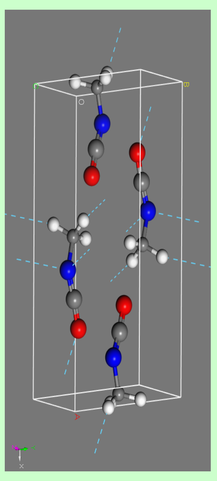

Fig. 1. Tentative structure of crystalline methyl isocyanate from DFT calculations [4]

We have recorded in our lab the IR spectra of amorphous CH_3NCO and CD_3NCO obtained by vapor deposition at 20 K. The most intense band corresponds to the NCO asymmetric stretching (ν_a-NCO). It has a characteristic quadruplet structure, usually attributed to the interaction with the CH_3 torsion. CD_3NCO was used to help the spectral assignment A phase transition from amorphous to crystalline methyl isocyanate is observed at ~ 90 K. The band strengths for the absorptions of CH_3NCO in ice at 20 K have also been measured.

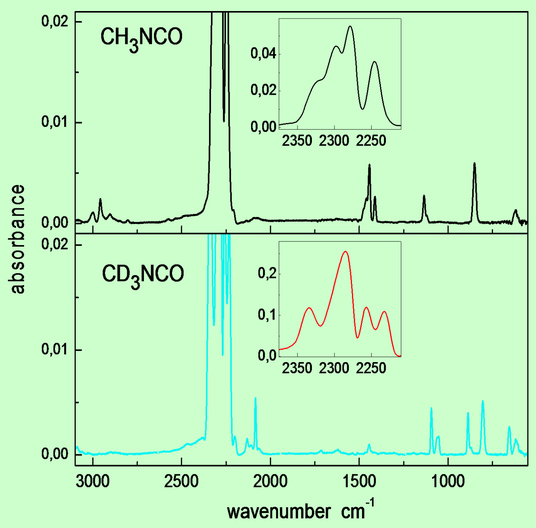

Fig.2. Infrared spectra of CH_3NCO and CD_3NCO

We have recorded spectra at a H_3NCO/H_2O ratio of 1.3%. The characteristic ν_a-NCO band is clearly recognizable. Its band strength (1.5×10^{-16} cm molec^{-1}) is comparable to that of pure CH_3NCO (see Table 1). The molecule is thus a good candidate for future astronomical searches, although the rest of the bands are probably too weak to be observable in space.

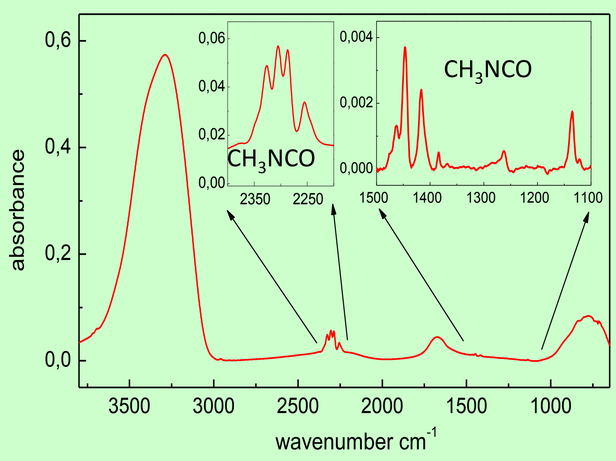

Fig. 3. IR spectrum of $H_3NCO(1.3\%)/H_2O$.

We have calculated the IR spectrum of the theoretical crystalline structure, and compared it with the experimental spectrum [4]. There is a good overall accord. The multiplet structure of the ν_a-NCO band is not reproduced in the calculated (harmonic) spectrum.

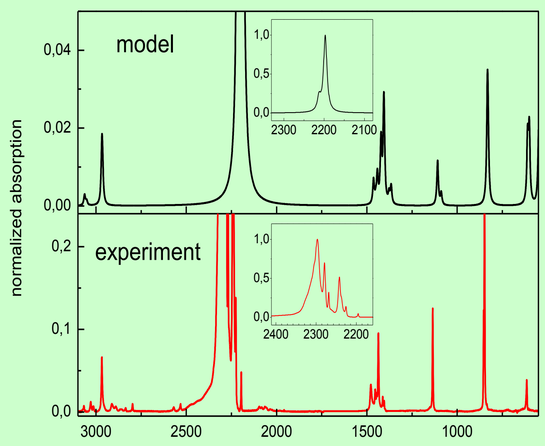

Fig. 4. Comparison of theoretical spectrum of the crystal with experiment.

Table 1. Assignment and bandstrengths for CH_3NCO

Peak (cm^{-1})	Wavenumber range (cm^{-1})	Wavelength range (μm)	A´ (cm molec^{-1})	band assignment
3000	3035-2979	3.29-3.36	8.8×10^{-19}	ν_a-CH_3
2958	2977-2930	3.36-3.41	1.4×10^{-18}	ν_s-CH_3
2278	2432-2160	4.11-4.63	1.3×10^{-16}	ν_a-NCO
1443	1492-1427	6.70-7.01	4.9×10^{-18}	δ_a-CH_3 + ν_s-NCO
1412	1428-1396	7.04-7.16	1.2×10^{-18}	δ_s-CH_3
1135	1076-1100	9.29-9.09	1.8×10^{-18}	r-CH_3
850	880-820	11.36-12.19	4.6×10^{-18}	ν-CN
616	670-550	14.92-18.18	1.4×10^{-18}	β-NCO

Conclusions

- The characteristic structure of the ν_a-NCO IR band and its high band strength indicate that CH_3NCO is a good candidate for searches in astronomical ices.
- The crystalline structure of CH_3NCO is assumed to be similar to that of HNCO.
- Both UV photons and electrons efficiently destroy CH_3NCO to yield CO, CO_2 and OCN^- . The final product distribution is similar for UV photons and 5 keV electrons. In the processing of CH_3NCO diluted in water ice, the product distribution is largely dominated by CO_2
- Electron bombardment is energetically more efficient than UV irradiation for the destruction of CH_3NCO diluted in water-ice.
- With the half-life doses derived in this work, CH_3NCO in the mantles of ice grains of dense clouds would be stable against UV radiation and relatively stable against CRs over the lifetime of a typical dense cloud (~10^7 yr).
- In contrast, CH_3NCO ice in a Kuiper belt object would be readily destroyed by the UV field and CRs at the surface, but would persist for ~10^9 yr at the sub-surface under 10 μm of water ice.

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Energetic processing

We have studied the stability of CH_3NCO under heating, UV irradiation with a D_2 lamp (UV photons ≈ 10.3-6.9 eV), and cosmic ray (CR) bombardment simulated with high energy electrons (5 keV). [5]
We have prepared samples of pure CH_3NCO and of CH_3NCO diluted in H_2O ice, formed by simultaneous deposition of both components at 20 K.
Heating of the ices leads to variations in the ν_a-NCO band profile but not to an appreciable depletion of CH_3NCO until H_2O sublimation (beyond T=150 K) and thus rules out hydrolysis in the ice.
UV irradiation and electron bombardment at 20 K lead to the disappearance of CH_3NCO and to the formation of CO, CO_2 and OCN^- in the processed ices.
The decay of the CH_3NCO concentration as a function of photon or electron fluence follows a first order kinetics. Destruction cross sections are in the 10^{-19} cm^2 range for UV photons and in the 10^{-16}-10^{-15} cm^2 range for electrons.

IR spectra monitoring

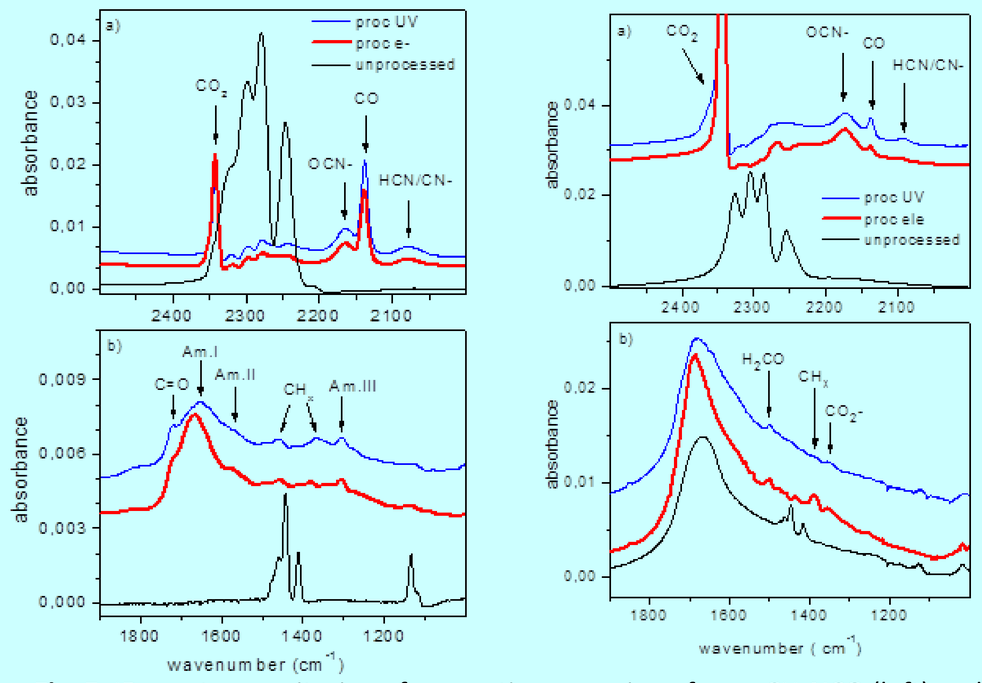

Fig. 5. IR spectra monitoring of energetic processing of pure CH_3NCO (left) and CH_3NCO/H_2O mixtures

Table 2 Column denstity of processed samples. All samples are deposited and processed at T=20 K

Sample	N(CH_3NCO) molec. cm^{-2}	N (H_2O) molec. cm^{-2}	Processing agent	φ (cm^{-2} s^{-1})
S1: CH_3NCO	$4.5\pm0.9 \times 10^{16}$	-------	UV (10.3-6.9 eV)	7.5×10^{13}
S2: CH_3NCO(4%)/H_2O	$2.5\pm0.5 \times 10^{16}$	$6.4\pm0.6 \times 10^{17}$	UV (10.3-6.9 eV)	7.5×10^{13}
S3: CH_3NCO	$4.3\pm0.9 \times 10^{16}$	---------	Electrons, 5 keV	4×10^{12}
S4: CH_3NCO(5%)/H_2O	$3.5\pm0.7 \times 10^{16}$	$6.5\pm0.6 \times 10^{17}$	Electrons, 5 keV	4×10^{12}

Sample processing

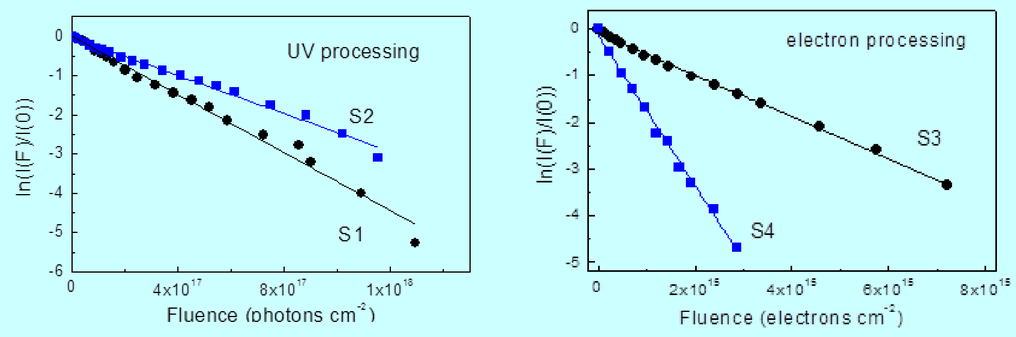

Fig. 6. Decay of the ν_a-NCO band as a function of photon fluence (UV processing) or electron fluence (electron processing): first order kinetics: **$\ln(I/I_0) = -\sigma F$**

Table 3. Summary of kinetics results

Sample	Processing agent	Destruction cross section, σ (cm^{-2})	Fraction of energy absorbed	Half-life doses, $D_{1/2}$ (eV molec^{-1})
S1: CH_3NCO	UV (10.3-6.9 eV)	$3.7\pm0.1 \times 10^{-18}$	0.15±0.03	5±2
S2: CH_3NCO(4%)/H_2O	UV (10.3-6.9 eV)	$2.4\pm 0.05\times 10^{-18}$	0.68±0.14	64±19
S3: CH_3NCO	Electrons, 5 keV	$4.5\pm0.1 \times 10^{-16}$	0.05±0.007	9±2
S4: CH_3NCO(5%)/H_2O	Electrons, 5 keV	$1.6\pm0.04 \times 10^{-15}$	0.30±0.04	18±5

Astrophysical processing of CH_3NCO in ice

Table 4. Estimated CH_3NCO half-life in dense clouds and cometary ices.

Location of ices in space	Lifetime of ices (yr)	Depth (cm)	UV Dose rate (eV molec^{-1} yr^{-1})	UV CH_3NCO half-life (yr)	CR Dose rate (eV molec^{-1} yr^{-1})	CR CH_3NCO half-life (yr)
Kuiper belt object (40 AU)	4.6×10^9	--- 10^{-3}	2.2×10^{-2}(a) -----	1.1×10^4 -----	5.6×10^{-3} (b) 1.6×10^{-8}(c)	3.2×10^3 1.1×10^9
Cold dense cloud	10^7	---	4×10^{-7}(d)	1.6×10^8	3×10^{-7}(d)	6×10^7

(a) Moore & Hudson 2005. IAU symposium 231, eds, D. C. Lis, G. S. Blake & E. Herbst. UV dose rates are estimated for the top 1.5×10^{-6} cm of the ice
(b) Cooper et al. 2003, EM&P, 92, 261. CR dose rate for ice thickness < 1×10^{-6} cm
(c) Strazzulla et al. 2003. CRPhy, 4, 791
(d) Moore et al. 2001. Spect Acta A, 57, 843. UV dose rates are estimated for typical grain mantles with a thickness of 2×10^{-6} cm

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