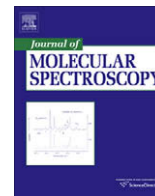


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Vibrational spectroscopy of *trans* and *cis* deuterated formic acid (HCOOD): Anharmonic calculations and experiments in argon and neon matrices

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ABSTRACT

The absorption spectra of *trans* and *cis* conformers of deuterated formic acid (HCOOD) isolated in argon and neon matrices are analyzed in the mid-infrared and near-infrared spectral regions (7900–450 cm⁻¹). Vibrational excitation by narrow-band IR radiation is used to convert the lower-energy *trans* conformer to the higher-energy *cis* form. A large number of overtone and combination bands are identified. The results of anharmonic vibrational calculations (CC-VSCF) for both conformers are reported and compared to the experimental spectra.

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1. Introduction

Formic acid exists in two planar forms differing by the O–H bond orientation with respect to the C–O bond with the 0° and 180° H–C–O–H dihedral angles (see Fig. 1). First unequivocal identification of the gas-phase absorption of the higher-energy *cis* form was made by analysis of rotational spectra which demonstrated that the *trans* conformer is lower in energy by ~1365 cm⁻¹ compared to the *cis* form [1]. The vibrational spectrum in the mid-IR region of *cis*-HCOOH was first obtained by Pettersson et al. in an argon matrix [2] and the detailed vibrational data on both forms of HCOOH in solid argon were reported later [3]. The preparation of *cis*-HCOOH was achieved by selective vibrational excitation which has been proved to be a powerful tool for promotion and investigation of conformational changes in cryogenic matrices [4].

The IR spectrum of *trans*-HCOOH is well known in matrices and in the gas phase. High-resolution measurements of all fundamental, many overtones and combination bands are available (see Ref. [5] and references therein) and an accurate assignment of the rotation–vibration spectral structure has been made with Fermi resonance taken into account [6]. Most of the fundamental bands of *trans*-HCOOD molecule were also recorded and analyzed in the gas phase [7] and in the matrices although the data for the overtone and combination transitions is sparse. The vibrational spec-

trum of *trans*-HCOOD measured in solid neon is close to that in the gas phase [8,9]. To the best of our knowledge, only one vibrational band of *cis*-HCOOH [COH torsion, 493.4205092(73) cm⁻¹] was measured in the gas phase [10]. Since the *cis* conformer is about 800 times less abundant at room temperature, the use of a multi-pass cell with total path length of 38.2 m was necessary to accumulate reliable absorption level [10].

The vibrational spectrum of *cis*-HCOOD is not studied in detail. The geometry and rotational constants of the ground state have been reported from the microwave studies in the gas phase for H¹²COOD and H¹³COOD [11,12]. The fundamental transitions for both conformers of HCOOD in different matrices are tabulated in Ref. [13], and a few combinations and overtones are assigned in Ref. [3]. The *cis*-HCOOH force field [14] might provide information about the transitions in *cis*-HCOOD because the potential energy function and the configuration of a molecule are practically unchanged upon isotopic substitution [15]. However, the work by Demaison et al. is mostly focused on *trans*-HCOOH and does not contain the force field for *cis*-HCOOH. It reports only the equilibrium geometry and rotational constants of the ground state of the *cis* conformer.

The present work supplies more information about *cis* and *trans*-HCOOD vibrational transitions, which complements the earlier studies [3,8,9,13]. The IR absorption spectra of *cis* and *trans*-HCOOD are measured in argon and neon matrices at 4.2 K. The anharmonic vibrational frequencies for the *trans* and *cis* conformers, derived from the correlation-corrected vibrational self-consistent-field calculations (CC-VSCF), are used for vibrational assignment of the overtone and combination bands.

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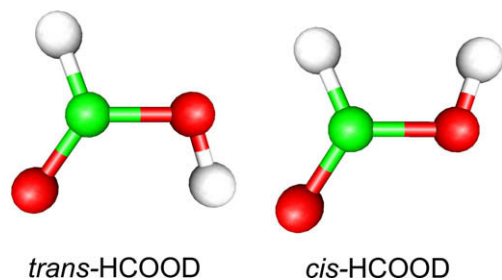


Fig. 1. *trans* and *cis* forms of formic acid. The notations follow Refs. [1–3].

2. Experimental

The gaseous samples were prepared by mixing deuterated formic acid HCOOD (IT Isotop, 95–98%), with argon or neon (AGA, 99.9999%), typically in 1:700 (Ar) and 1:1000 (Ne) proportions in a glass bulb. The matrices were deposited onto a CsI substrate at 18 K for Ar and at 4.2 K for Ne matrices in a closed cycle helium cryostat (Sumitomo Heavy Industries). The IR absorption spectra ($7900\text{--}450\text{ cm}^{-1}$) were measured with a Nicolet SX-60 FTIR spectrometer at 4.2 K. The spectral measurements in mid-IR region were carried out with the resolution of 0.25 cm^{-1} using a cooled MCT detector and KBr beamsplitter, and the near-IR spectra were recorded using a cooled InSb detector and quartz beamsplitter with spectral resolution of 0.5 cm^{-1} . Typically 500 interferograms were co-added.

trans-HCOOD was converted to the *cis* form by optical excitation of the first OD stretching overtone at 5174.5 cm^{-1} in a neon matrix and at 5149.7 cm^{-1} in an argon matrix with pulse energy density of $\sim 1\text{ mJ/cm}^2$. For argon matrices, excitation at 4382.0 cm^{-1} ($\nu\text{OD} + \nu\text{C=O}$ combination) was also used. An optical parametric oscillator (OPO Sunlite with IR extension, Continuum) was used as a source of pulsed IR radiation. A Burleigh WA-4500 wavemeter measured the OPO signal wavelength providing an absolute accuracy better than 1 cm^{-1} in the IR region.

3. Computational method

The computational method was essentially the same as described in our previous work [3]. The equilibrium structures of *trans*- and *cis*-HCOOD were calculated using the second-order Møller–Plesset perturbation (MP2) theory with the 6-311++G(2d,2p) basis set. This basis set reproduces the experimental structural and vibrational properties of *trans* formic acid with an acceptable accuracy [16,17]. The anharmonic vibrational properties of *trans*- and *cis*-HCOOD were studied by combining the electronic ab initio code GAMESS [18] with the vibrational self-consistent field (VSCF) method and its extension by corrections via second-order perturbation theory [19–23].

4. Assignment and discussion

In this section, we analyze the mid- and near-IR ($450\text{--}7900\text{ cm}^{-1}$) spectra of the *trans* and *cis* conformers of deuterated formic acid in argon and neon matrices and compare them with the computational and, when possible, with gas-phase spectra. The bands of *trans*-HCOOD dominate in the spectrum after deposition. An efficient *trans* to *cis* conversion ($>90\%$) was achieved by excitation of the OD stretching overtone or the $\nu\text{OD} + \nu\text{C=O}$ combination (see Fig. 2). *cis*-HCOOD has a larger lifetime compared to *cis*-HCOOH because the tunneling to the *trans* form is slowed down by deuteration [13,24,25], and their increased stability allows accurate data collection of *cis*-HCOOD.

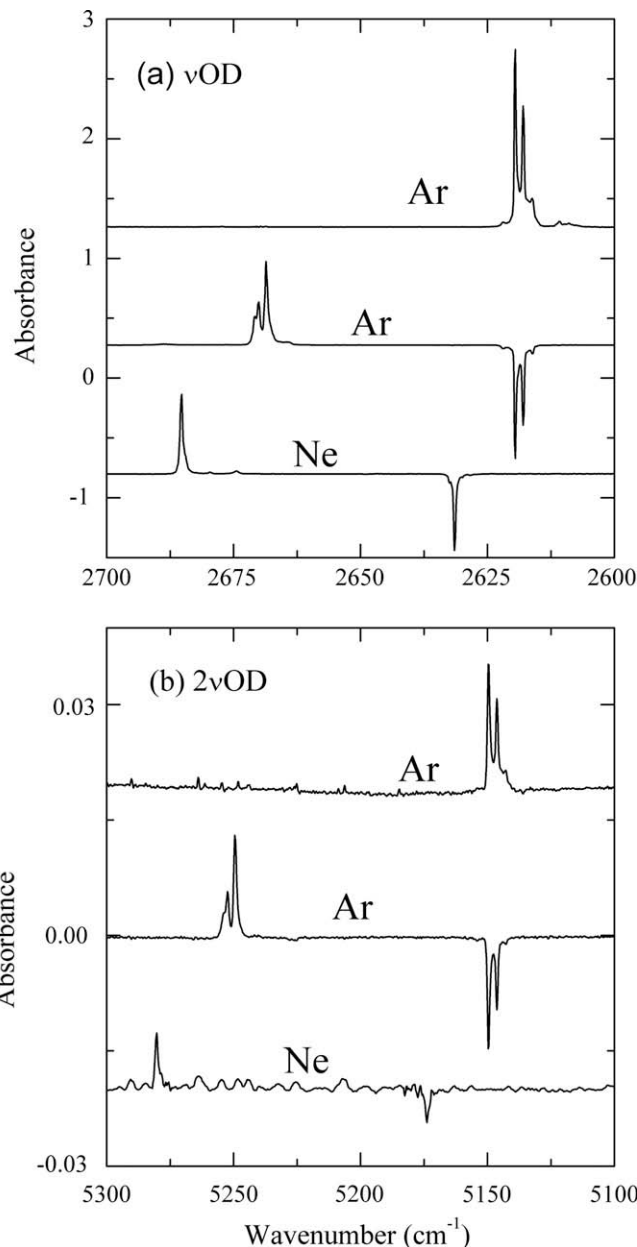


Fig. 2. (a) The OD stretching bands and (b) the OD stretching overtones of HCOOD in Ar and Ne matrices at 4.2 K. The as-deposited matrices mainly contain the *trans* conformer as shown for an argon matrix (upper traces). Vibrational excitation converts *trans*-HCOOD to *cis*-HCOOD as presented by the difference spectra (middle and lower traces).

In a neon matrix, the bands are mostly single absorption peaks, and their frequencies are close to the gas-phase values [8]. In an argon matrix, the band splitting due to two matrix trapping sites is observed similarly to HCOOH [3]. Table 1 presents the observed absorption bands for the *trans* and *cis* conformers of HCOOD in argon and neon matrices and the anharmonic computational frequencies together with the available gas-phase data.

4.1. Fundamental transitions

The literature data [7,8,13,26,27] allows a straightforward assignment of the fundamental bands of *trans*-HCOOD. The fundamental transitions of the *cis* form are relatively easy to assign as well (see Ref. [13]). In Fig. 2(a), the HCOOD spectra in the OD

Table 1

Observed experimental vibrational frequencies (cm^{-1}) for *trans*- and *cis*-HCOOD in Ar and Ne matrices at 4.2 K, CC-VSCF calculated anharmonic vibrational frequencies (intensities in parentheses in km/mol) and gas-phase data.

Assignment	<i>trans</i> -HCOOD				<i>cis</i> -HCOOD		
	Calculated	Gas ^a	Ar	Ne	Calculated	Ar	Ne
τCOD	497.5 (103.1)	507.5	505.2s 506.7s	506.9s	361.4 (29.3)	–	–
$\text{OCO}-\text{CODdef.}$	555.7 (52.2)	560.2	558.7m 559.7s	557.9m	621.5 (17.9)	633.0m 633.6m	629.4m
δCOD	972.7 (86.2)	972.8	970.0m 970.6s	971.1s	897.9 (7.0)	910.5m 911.2w	906.8m
$2\tau\text{COD}$	960.9 (4.2)	1011.7	1008.3m 1009.4m	1009.5m	688.3 (0.16)	740.4vw	746.2vw
ωCH	1033.2 (0.1)	–	1035.1vw 1036.4vw	1037.3vw	1014.4 (1.0)	1041.2vw	1039.3vw
$\nu\text{C}-\text{O}$	1163.7 (206.1)	1177.1	1181.7vs	1176.9vs	1140.9 (348.2)	1164.0vs	1159.0vs
γCH	1381.1 (7.2)	1368	1371.1vw 1374.3vw	1367.9w	1403.6 (2.7)	1391.0vw 1395.4vw	1388.0vw
$\tau\text{COD} + \delta\text{COD}$	1441.0 (0.0)	–	1427.5vw	1433.0vw	1207.8 (0.0)	–	–
$\text{OCO}-\text{CODdef} + \delta\text{COD}$	1533.5 (0.1)	–	–	1526.3vw	1524.9 (0.1)	1543.2vw	1534.2vw
$\text{OCO}-\text{CODdef} + \nu\text{C}-\text{O}$	1715.6 (3.7)	1732.1	1735.7w	1730.0w	1760.7 (0.8)	–	–
$\nu\text{C}=\text{O}$	1751.3 (460.8)	1773.6	1765.6vs 1767.2vs	1771.0vs	1789.5 (434.2)	1788.9m ^b 1799.3vs ^b 1821.0m ^b	1781.2w ^b 1798.9vs ^b 1818.2vs ^b
$2\delta\text{COD}$	1938.0 (0.3)	–	1949.7vw	1950.6vw	1779.9 (0.1)	–	–
$\omega\text{CH} + \delta\text{COD}$	2004.8 (0.0)	–	2008.4vw	2008.6vw	1912.3 (0.0)	–	–
$\nu\text{C}-\text{O} + \delta\text{COD}$	2129.6 (3.7)	–	2144.1w 2181.0w	2139.8w 2176.8w	2030.1 (2.1)	2065.1w	2055.2w
$\nu\text{C}-\text{O} + \omega\text{CH}$	2193.7 (0.1)	–	2194.7vw	2192.9vw	2151.8 (0.1)	–	–
$2\nu\text{C}-\text{O}$	2311.0 (0.9)	–	2349.4vw	2341.1vw	2264.7 (4.5)	2314.7vw	2301.5vw
νOD	2625.6 (67.4)	2631.4	2618.0s 2619.5s	2631.5s	2677.4 (128.6)	2668.7s 2670.0m	2685.5s
$\nu\text{C}=\text{O} + \delta\text{COD}$	2720.2 (2.5)	–	2723.1vw	2716.6vw	2684.7 (2.1)	2688.7vw	2674.4vw
$\nu\text{C}=\text{O} + \omega\text{CH}$	2776.4 (0.2)	–	2732.1vw 2728.7w	2737.9w	2795.8 (0.2)	2752.0w 2758.2vw	2742.8w 2724.9vw
$\nu\text{C}=\text{O} + \nu\text{C}-\text{O}$	2914.8 (1.9)	–	2940.7w	2935.5m	2929.8 (2.4)	–	2939w
νCH	2952.8 (29.7)	2942	2961.2m	2951.9m	2861.4 (47.4)	2895.3m 2897.9m	2872.7m
$\nu\text{OD} + \tau\text{COD}$	3104.4 (10.0)	–	3123.3vw 3125.8vw	3136.7w 3138.1vw	3008.1 (7.6)	3050.6vw	3059.2vw
$\nu\text{C}=\text{O} + \gamma\text{CH}$	3126.5 (0.4)	–	3134.8vw 3139.5vw	–	3186.9 (0.1)	–	–
$\nu\text{OD} + \text{OCO}-\text{CODdef}$	3139.3 (0.5)	–	3171.2vw 3173.9vw	3183.0vw	3240.4 (0.3)	–	–
$2\nu\text{C}=\text{O}$	3483.9 (4.5)	–	3512.9vw 3522.0vw	3524.1w 3529.1vw	3553.7 (4.6)	3571.1vw 3577.3vw	3582.2w 3583.2vw 3598.8w
$\nu\text{OD} + \omega\text{CH}$	3628.6 (0.0)	–	–	3601.3vw	3647.4 (0.0)	–	3629.4vw
$\nu\text{OD} + \nu\text{C}-\text{O}$	3754.7 (0.0)	–	3736.1vw	3728.7vw	3760.4 (3.9)	3741.5vw	3740.2vw
$\nu\text{CH} + \nu\text{C}-\text{O}$	4114.4 (1.3)	4125	4140.1vw	4123.8vw	4001.5 (1.4)	4052.4vw 4058.3vw	4025.9vw
$\nu\text{OD} + \nu\text{C}=\text{O}$	4345.8 (0.5)	4404	4382.0vw	4399.5vw	4418.2 (0.3)	–	–
$\nu\text{CH} + \nu\text{C}=\text{O}$	4704.3 (1.8)	4719	4720.7vw 4723.8vw	4714.2vw	4653.6 (2.1)	4687.9vw 4707.9vw	4666.7vw 4686.8vw
$2\nu\text{OD}$	5163.6 (1.1)	5181	5146.3vw 5149.7w	5174.5vw	5284.7 (1.1)	5249.5w 5252.4vw	5280.4vw
$2\nu\text{CH}$	5791.3 (0.5)	–	5152.9vw 5801.7vw	5769.3vw	5690.9 (0.5)	5253.7vw 5592.9vw 5594.4vw	5548.6vw

^a From Refs. [7,11,26,27,29].

^b Components of Fermi resonance.

stretching region are presented. The band at 2631.5 cm^{-1} is the OD stretching mode (νOD) of *trans*-HCOOD in a neon matrix. It shows good agreement with the anharmonic calculations yielding 2625.6 cm^{-1} . For *cis*-HCOOD, this mode shifts to 2685.5 cm^{-1} (computationally to 2677.4 cm^{-1}). In an argon matrix, the *trans*- and *cis*-HCOOD νOD absorptions are at 2618.0 and 2668.7 cm^{-1} , showing a typical matrix shift from the neon matrix values.

The CC-VSCF calculations reproduce well the experimental frequencies for most of the fundamental modes. The calculated intensities of HCOOD match the experimental values (see Fig. 3). Similarly good agreement between the anharmonic calculations and the experimental spectra was reported for HONO [28]. The

high-frequency OD and CH stretching modes for the *trans* conformer, where anharmonicity is significant, are obtained with the 0.3% inaccuracy compared to the gas-phase data. For the torsional mode the anharmonic calculations and the experimental frequencies from the gas-phase experiments agree better for the deuterated molecule than for that of HCOOH ($\sim 2\%$ error for *trans*-HCOOD, $\sim 7\%$ for *trans*-HCOOH). This is explained by the fact that the vibrational amplitude is smaller for HCOOD and the limitation of large-amplitude vibrational mode description by the CC-VSCF method becomes less important.

Among other fundamental modes, the largest difference between the calculated and experimental neon matrix values is ob-

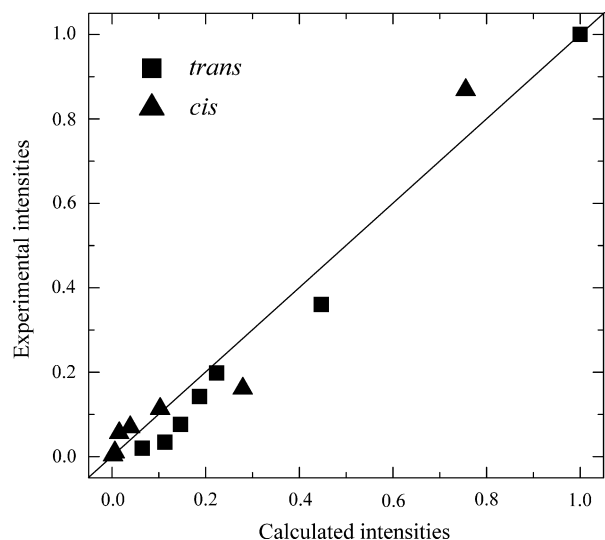


Fig. 3. Relative calculated and experimental intensities for the fundamental modes of HCOOD. The intensities are normalized by the $\nu\text{C}=\text{O}$ intensity of *trans*-HCOOD. The experimental values are obtained in a neon matrix. The straight line shows 1:1 agreement with the experiment.

served for the C–O stretching and CH-wagging vibrations of the *cis* conformer ($\sim 20\text{ cm}^{-1}$, $\sim 2\%$). For the $\nu\text{C}=\text{O}$ vibration, this discrepancy possibly originates from the fact that the CC-VSCF method accounts only for pairwise couplings and the multiple interactions are neglected [19–21]. The $\nu\text{C}=\text{O}$ vibration is a mixed mode and the contribution of the OCO–COD deformational motion is large [8]. The reason for the difference between the calculated and experimental frequencies of the CH-wagging mode remains an open question because this vibrational mode is well-isolated [8].

The assignment of vibrational transitions in the $\nu\text{C}=\text{O}$ region is less certain due to Fermi resonances. An accurate analysis of the $\nu\text{C}=\text{O}$ vibration of *trans*-HCOOD in the gas phase yields that the strongest perturbation for the $\nu\text{C}=\text{O}$ vibrational state arises from the nearest OCO–CODdef + $\nu\text{C}=\text{O}$ combination. The energy difference between these levels is about 40 cm^{-1} [7]. Another combination state ($\nu\text{C}=\text{O} + \tau\text{COD}$) perturbs the $\nu\text{C}=\text{O}$ level in a considerably weaker extent because the energy gap between the levels is $\sim 90\text{ cm}^{-1}$. The key role of the $\nu\text{C}=\text{O} + \tau\text{COD}$ state is the perturbation of the OCO–CODdef + $\nu\text{C}=\text{O}$ state [7]. In the case of *cis*-HCOOD, one may expect that the influence of the $\nu\text{C}=\text{O} + \tau\text{COD}$ combination on the $\nu\text{C}=\text{O}$ state gets even smaller due to the increasing energy gap between the interacting levels, but the first overtone of the δCOD bending vibration (computationally at 1779.9 cm^{-1}) might play an important role on the frequency and intensity of the $\nu\text{C}=\text{O}$ band as well as the OCO–CODdef + $\nu\text{C}=\text{O}$ and $\gamma\text{CH} + \tau\text{COD}$ combinations (computationally at 1760.7 and 1761.5 cm^{-1} , respectively). The different “partners” of the Fermi resonance in the *cis* and *trans* molecules might be responsible for the significant different spectra of the two conformers in this region.

The $\nu\text{C}=\text{O}$ vibration of *trans*-HCOOD in a neon matrix has a single absorption shifted from the gas-phase value by -2.6 cm^{-1} and in an argon it is a doublet due to the matrix site effect which is shifted by -6.4 and -8.2 cm^{-1} from the gas-phase value. Similar doublet was observed for *trans*-HCOOH in an argon matrix [3]. The OCO–CODdef + $\nu\text{C}=\text{O}$ combination is observed $\sim 40\text{ cm}^{-1}$ below (1730.0 cm^{-1} in a Ne matrix) in agreement with the gas-phase values.

A triplet structure is observed in the $\nu\text{C}=\text{O}$ region of *cis*-HCOOD in various matrices [13]. The intensity distribution is strikingly different for different matrices: the triplet intensity ratio is 1:7:6 in a neon matrix and 3:6:2 in an argon matrix. The presumably inter-

acting combinations are predicted to be ~ 1000 smaller in intensity than the fundamental transition, so that the comparable values of the experimentally observed peaks suggest that the Fermi interaction actually takes place. The precise assignment of the triplet components remains an open question and exceeds the scope of the present work.

The computed intensities of the fundamental transitions agree very well with the experimental values (see Fig. 3). The strongest absorption is the *trans* C=O stretching vibration both computationally and experimentally. This allows us to relay to some extent on the calculated intensities, in addition to the frequency values, for assignment of overtones and combinations.

4.2. Overtone and combination transitions

A number of overtones and combination bands are observed and identified in the mid- and near-IR regions. The assignment of the overtones and combinations is based on the anharmonic CC-VSCF calculations. The experimentally observed and calculated vibrational frequencies are collected in Table 1.

As an example, Fig. 2(b) presents the first OD stretching overtone of *trans*- and *cis*-HCOOD in argon and neon matrices. The $2\nu\text{OD}$ band of *trans*-HCOOD is observed in a neon matrix at 5174.5 cm^{-1} and predicted by the calculations at 5163.6 cm^{-1} , which is in good agreement with the gas-phase value (5181 cm^{-1}) [11]. For *cis*-HCOOD, the $2\nu\text{OD}$ absorption is predicted at 5284.7 cm^{-1} and observed at 5280.4 cm^{-1} in a neon matrix. The $2\nu\text{OD}$ bands are shifted to 5149.7 (*trans*) and 5249.5 cm^{-1} (*cis*) in an argon matrix.

If the $\nu\text{C}=\text{O}$ stretching vibration is involved in a combination transition, the resulting spectrum of the *cis* form might show a characteristic splitting (ca. 20 cm^{-1}) due to the Fermi resonance in the fundamental region. For example, a very weak doublet at 4686.8 and 4666.7 cm^{-1} in a neon matrix and at 4687.9 and 4707.9 cm^{-1} in an argon matrix is assigned to the $\nu\text{CH} + \nu\text{C}=\text{O}$ combination mode for *cis*-HCOOD. The *trans*-HCOOD absorption band at 4714.2 cm^{-1} (Ne) and 4720.7 cm^{-1} (Ar) is assigned to the $\nu\text{CH} + \nu\text{C}=\text{O}$ combination. In the gas-phase spectrum, this combination was observed at 4719 cm^{-1} for *trans*-HCOOD [11].

In the previous work, the doublet at 2753.4 and 2759.9 cm^{-1} was tentatively assigned to the $\nu\text{C}=\text{O} + 2\tau\text{COH}$ combination of *cis*-HCOOH in an argon matrix [3]. Two bands at 2752.0 and 2758.0 cm^{-1} appear in the present spectra of *cis*-HCOOD. We reconsider the earlier assignment because the absorptions under question show negligible isotopic shifts whereas the $\nu\text{C}=\text{O} + 2\tau\text{COH}$ combination should be sensitive to the isotopic substitution with a shift of $\sim 300\text{ cm}^{-1}$. We suggest that the combination transition $\nu\text{C}=\text{O} + \omega\text{CH}$ gives rise to this doublet in the spectrum of *cis*-HCOOD in an argon matrix. The corresponding band of *trans* form appear $\sim 20\text{ cm}^{-1}$ lower in frequency in agreement with the calculations. The calculated values are 2795.8 cm^{-1} for *cis*- and 2776.4 cm^{-1} for *trans*-HCOOD.

A weak absorption at 2716.6 cm^{-1} (Ne) and 2723.1 cm^{-1} (Ar) probably belongs to the $\nu\text{C}=\text{O} + \delta\text{COD}$ combination mode of the *trans* molecule (computed at 2720.2 cm^{-1}). The corresponding band of the *cis* form is found $\sim 30\text{ cm}^{-1}$ lower in frequency in agreement with the calculations. The bands of *trans*-HCOOD at 2778.6 cm^{-1} (Ne) and at 2773.2 and 2782.5 cm^{-1} (Ar) might belong to the $\nu\text{C}=\text{O} + 2\tau\text{COD}$ mode although we do not have a theoretical estimate for this frequency.

Several other absorptions also admit multiple assignments. There are two doublets of *trans*-HCOOD at 3123.3 , 3125.8 cm^{-1} and at 3134.8 , 3139.5 cm^{-1} in argon matrices, whose assignment is not certain. Two combination modes of *trans*-HCOOD are expected to absorb in this region: the $\nu\text{OD} + \tau\text{COD}$ mode (computed at 3104.4 cm^{-1}) and the $\nu\text{C}=\text{O} + \gamma\text{CH}$ mode (computed at 3126.5 cm^{-1}). We tentatively assign two peaks at 3123.3 and 3125.8 cm^{-1} to the $\nu\text{OD} + \tau\text{COD}$ mode

because they are lower in frequency than the other pair which makes a better agreement with the calculations. The corresponding peaks in a neon matrix are significantly shifted to higher frequencies (3136.7 and 3138.1 cm^{-1}) as it should be for this combination whereas the $\nu\text{C}=\text{O} + \gamma\text{CH}$ mode should demonstrate only a small shift (if any) due to the opposite matrix-induced shifts of the $\nu\text{C}=\text{O}$ and γCH fundamentals. The $\nu\text{OD} + \tau\text{COD}$ bands of the *cis* form is found substantially lower in frequency [3050.6 (Ar) and 3059.2 cm^{-1} (Ne)] in agreement with calculations (3008.1 cm^{-1}). The other doublet (3134.8, 3139.5 cm^{-1}) probably originates from the $\nu\text{C}=\text{O} + \gamma\text{CH}$ combination of *trans*-HCOOD. The $\nu\text{C}=\text{O} + \gamma\text{CH}$ band of *cis*-HCOOD is predicted at higher frequencies (3186.9 cm^{-1}), and it is not found due to its weakness.

For *trans*-HCOOD, the bands at 3524.1 and 3529.1 cm^{-1} in a neon matrix cannot be unambiguously distinguished between the $\nu\text{C}=\text{O}$ overtone and the $\nu\text{OD} + \delta\text{COD}$ combination. We tend to assign these bands and the corresponding absorptions of *cis*-HCOOD at 3582.2 and 3598.8 cm^{-1} to the $2\nu\text{C}=\text{O}$ mode since they show a characteristic splitting of the $\nu\text{C}=\text{O}$ fundamental region. In addition, the $\nu\text{OD} + \delta\text{COD}$ absorption of the *cis* form is expected at significantly lower frequencies (calculated at 3492.5 cm^{-1}) and ~ 10 times smaller in intensity while we observe a blue shift of the *cis* absorptions and comparable intensities.

For very weak bands of the *trans* conformer at 1949.7 and 1950.6 cm^{-1} in argon and neon matrices two plausible assignments are suggested by the calculations: $2\delta\text{COD}$ (1938.3 cm^{-1}) and $\text{OCO}-\text{CODdef} + \gamma\text{CH}$ (1938.3 cm^{-1}). Nevertheless, several arguments favor the assignment to $2\delta\text{COD}$. For $\text{OCO}-\text{CODdef} + \gamma\text{CH}$, the experimental coupling constants have unrealistically large positive values (ca. +20 cm^{-1}) whereas the anharmonicity constants for $2\delta\text{COD}$ are +4.2 cm^{-1} for both matrices which is more reasonable. Moreover, the computed intensity of the $2\delta\text{COD}$ mode is higher than for the other candidate. The $2\delta\text{COD}$ band of *cis*-HCOOD cannot be unambiguously assigned because it is predicted in the $\text{C}=\text{O}$ stretching region and probably participates in the Fermi resonance mentioned above.

A few absorptions are observed only for one conformer. The bands at 4399.5 cm^{-1} in neon and 4382.0 cm^{-1} in argon matrices

are assigned to the $\nu\text{OD} + \nu\text{C}=\text{O}$ combination of the *trans* form, which is predicted by calculations at 4345.8 cm^{-1} . The $\nu\text{C}-\text{O} + \omega\text{CH}$ combination band of *trans*-HCOOD (calculated at 2193.7 cm^{-1}) is observed at 2192.9 cm^{-1} in neon and at 2194.7 cm^{-1} in argon matrices. These modes are not observed for *cis*-HCOOD supposedly due to their weakness.

The computed CC-VSCF frequencies for the bands, which were not detected in the spectra, are collected in Table 3. Most of these modes are computationally very weak (<0.5 km/mol). The torsional mode for *cis*-HCOOD most probably lies below our measurement limit of 450 cm^{-1} . The expected positions of some combination bands or overtones are close to intense fundamentals, which complicate their detection. For example, the $2\text{OCO}-\text{CODdef}$ band for *trans*-HCOOD should be at $\sim 1110 \text{ cm}^{-1}$, which coincides with the $\nu\text{C}-\text{O}$ stretching region.

There are small discrepancies with the previously published data (see Table 3 in Ref. [3]). We suppose that the observed frequency deviations of 1–2 cm^{-1} are due to relatively high inaccuracy for the high-frequency region and differences in sample preparations. A relatively poor signal-to-noise ratio impeded to find two peaks at 4142.6 and 4380.2 cm^{-1} reported previously for the $\nu\text{CH} + \nu\text{C}-\text{O}$ and $\nu\text{OD} + \nu\text{C}=\text{O}$ modes in an argon matrix [3].

4.3. Anharmonicity and coupling constants

Table 2 shows coupling and anharmonicity constants of for *trans*- and *cis*-HCOOD which are calculated by the formulas [15]:

$$x_{ij} = v_{i+j} - v_i - v_j \quad (1)$$

$$x_{ii} = \frac{1}{2}(v_{2i} - 2v_i). \quad (2)$$

Here v_i and v_j are the fundamental frequencies, v_{2i} is the overtone frequency, v_{i+j} is the combination frequency, x_{ij} is the coupling constant, and x_{ii} is the anharmonicity constant. The corresponding results for *trans*- and *cis*-HCOOH were previously reported by Maçõas et al. [3].

Table 2

Experimental and CC-VSCF calculated anharmonicity and coupling constants (in cm^{-1}) for *trans*- and *cis*-HCOOD in gas phase, argon and neon matrices.

	<i>trans</i> -HCOOD				<i>cis</i> -HCOOD		
	Ar	Ne	Gas ^a	Calc	Ar	Ne	Calc
<i>Combinations</i>	<i>Coupling constants</i> (x_{ij})						
OCO–CODdef. + νOD	–5.5	–6.4		–42.0			–58.5
OCO–CODdef. + $\nu\text{C}-\text{O}$	–5.7	–4.8	–5.2	–3.8			–1.7
$\delta\text{COD} + \text{OCO}-\text{CODdef.}$		–2.7		+5.1	–0.9	–2.0	+5.5
$\delta\text{COD} + \omega\text{CH}$	+1.4	+0.2		–1.1			0.0
$\delta\text{COD} + \nu\text{C}-\text{O}$	–8.2	–8.2		–6.8	–9.4	–10.6	–8.7
$\delta\text{COD} + \tau\text{COD}$	–47.6	–45.0		–29.2			–51.5
$\delta\text{COD} + \nu\text{C}=\text{O}$	–21.2	–19.0		–3.8	–21.1	–31.3	–2.7
$\nu\text{C}-\text{O} + \omega\text{CH}$	–23.4	–21.3		–3.2			–3.5
$\nu\text{C}-\text{O} + \nu\text{OD}$	–65.1	–79.7		–34.6	–91.2	–104.3	–57.9
$\nu\text{C}-\text{O} + \nu\text{CH}$	–2.8	–5.0	–4.9	–2.1	–9.5	–5.8	–0.8
$\nu\text{C}=\text{O} + \nu\text{C}-\text{O}$	–6.6	–12.4		–0.2			–0.6
$\nu\text{C}=\text{O} + \omega\text{CH}$	–26.7	–29.7		–8.1			–8.1
$\nu\text{C}=\text{O} + \nu\text{OD}$	–1.6	–3.0	–1.0	–31.1			–48.7
$\nu\text{C}=\text{O} + \nu\text{CH}$	–6.1	–8.7	–13.0	+0.2			–2.7
$\nu\text{C}=\text{O} + \gamma\text{CH}$	–3.5			–5.9			–6.2
$\nu\text{OD} + \tau\text{COD}$	–1.4	–1.7		–18.7			–30.7
$\nu\text{OD} + \omega\text{CH}$		–67.5		–30.2		–95.4	–44.4
<i>Overtones</i>	<i>Anharmonicity constants</i> (x_{ii})						
$2\nu\text{CH}$	–60.4	–67.3		–57.2	–98.9	–98.4	–15.9
$2\nu\text{OD}$	–44.9	–44.3	–40.9	–43.8	–43.9	–45.3	–35.1
$2\nu\text{C}=\text{O}$	–9.35	–9.35		–9.35	–13.75	–7.3 ^b	–12.6 ^b
$2\nu\text{C}-\text{O}$	–7.0	–6.4		–8.2	–5.15	–8.1	–8.5
$2\delta\text{COD}$	+4.2	+4.2		–3.7			–7.9
$2\tau\text{COD}$	–1.1	–2.1	–1.6	–17.0			–17.3

^a From Refs. [7,11,26,27,29].

^b Values for the most intensive component of $\nu\text{C}=\text{O}$ band (1798.9 in Ne and 1799.3 cm^{-1} in Ar).

Table 3

CC-VSCF vibrational frequencies (cm^{-1}) of non-observed absorptions for the *trans*- and *cis*-HCOOD. Calculated intensities in km/mol are given in parentheses.

Assignment	<i>trans</i> -HCOOD	<i>cis</i> -HCOOD
OCO—CODdef + τ COD	1038.7 (0.2)	950.0 (0.0)
2OCO—CODdef	1107.0 (0.1)	1231.4 (0.0)
ω CH + τ COD	1533.2 (0.1)	1378.9 (0.2)
OCO—CODdef + ω CH	1588.4 (0.0)	1634.8 (0.0)
ν C—O + τ COD	1653.7 (0.0)	1479.7 (0.2)
γ CH + τ COD	1877.2 (0.0)	1761.5 (0.0)
OCO—CODdef + γ CH	1938.3 (0.0)	2026.9 (0.0)
ν C=O + τ COD	2245.6 (0.1)	2145.6 (0.0)
γ CH + δ COD	2354.1 (0.0)	2303.2 (0.1)
ν C—O + γ CH	2542.8 (0.0)	2540.8 (0.1)
2 γ CH	2760.9 (0.7)	2980.1 (0.9)
ν CH + τ COD	3447.4 (0.0)	3220.0 (0.1)
ν CH + OCO—CODdef	3509.6 (0.1)	3481.8 (0.1)
ν OD + δ COD	3535.4 (2.0)	3492.5 (0.3)
ν CH + ω CH	3923.4 (0.0)	3816.5 (0.1)
ν CH + δ COD	3926.9 (0.0)	3760.7 (0.1)
ν OD + γ CH	3975.5 (0.1)	4035.1 (0.0)
ν CH + γ CH	4275.8 (0.4)	4208.0 (0.1)

It is seen from Table 2 that the CC-VSCF calculations reproduce very well the anharmonic properties of the overtone transitions (with an exception of the 2τ COD mode) although they are somewhat less precise for the *cis* form. The absolute value of the anharmonicity constant for the 2ν OD band is about two times smaller than for 2ν OH [3], and the agreement with the gas-phase data is good.

The calculated coupling constants show poorer agreement with the experimental results. For most of the bands (δ COD + ν C=O, ν C—O + ν OD, etc.) the experimental coupling constants for both matrix hosts and the gas phase (when available) are larger than the predicted value, which demonstrate that the calculations underestimate the anharmonicity effect for HCOOD. The calculated coupling constants appear overestimated only for the OCO—CODdef. + ν OD and ν C=O + ν OD combination modes. The opposite trend was observed for HCOOH, where most of the coupling constants were overestimated [3].

The COD bending mode has unusual properties. The 2δ COD overtone has positive experimental anharmonicity constant ($+4.2 \text{ cm}^{-1}$ for both matrices) whereas the calculations predict a negative value of -3.7 cm^{-1} . The δ COD + ω CH combination band also has positive experimental coupling constants, and two combinations (δ COD + OCO—CODdef and ν C=O + γ CH) demonstrate the positive values of calculated coupling constants. We assume that the Fermi resonance of δ COD and the overtone of the τ COD mode in *trans*-HCOOD [27] might be at least partly responsible for the peculiarities of the δ COD mode.

Except for the ν C=O + ν CH vibration, no significant differences between experimental anharmonicity and coupling constants in matrices and the gas phase are observed which means that the geometries and the electronic properties of the molecules are not significantly perturbed by matrix hosts.

5. Conclusions

The vibrational spectra of *trans*- and *cis*-HCOOD in neon and argon matrices are studied in the $7900\text{--}450 \text{ cm}^{-1}$ region. Most of the

relatively strong combination and overtone modes predicted by the CC-VSCF method are detected in matrices. The fundamental frequencies and intensities are well reproduced by the CC-VSCF calculations. The calculated combination and overtones frequencies show sometimes a considerable shift from the experimental values up to $\sim 50 \text{ cm}^{-1}$, nevertheless, the relative error does not exceed $\sim 3\%$. The near- and mid-IR data for *cis*-HCOOD in a neon matrix is reported here for the first time.

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