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He I photoelectron spectroscopy of formic acid isotopomers HCOOH and DCOOD

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Abstract

He I photoelectron spectra (PES) of HCOOH and DCOOD have been measured with an electron kinetic energy resolution of 15 meV. Analysis of observed vibronic structure in the two PES bands in the 11.3–13.5 eV energy region provided values for several vibrational modes of the $\tilde{X}\,^2A'$ and $\tilde{A}\,^2A''$ electronic states of $HCOOH^+$ and $DCOOD^+$. This analysis is based on the implications of structural changes expected to occur on ionization, using literature values for calculated geometries of these states. The vibronic assignments of both PES bands were consistent with isotopic effects on vibrational mode frequencies and were helped by considerations on relations between carbon–oxygen bond lengths and stretch mode frequencies. The analysis of the second PES band indicates that the calculated structure of the $\tilde{A}\,^2A''$ state of the ion requires more refined theoretical treatment. The PES first ionization energy of HCOOH agrees well with that obtained from Rydberg series in absorption spectra, and values more precise than hitherto were obtained for the first and second ionization energies of DCOOD, 11.335 ± 0.002 eV and 12.380 ± 0.002 eV respectively, and the second ionization energy of HCOOH, 12.378 ± 0.002 eV.

1. Introduction

Formic acid is closely related to the possible building blocks of biomolecules [1] so that its properties are of direct interest for radioastronomy searches and for exobiology studies. As part of an extensive study of the spectroscopic and photophysical properties of formic acid we have had occasion to investigate the He I photoelectron spectra of HCOOH and its isotopomer DCOOD at a higher resolution than that of previous photoelectron spectra (PES) studies. The results on the first (band I) and second (band II) photoelectron bands, respectively associated with formation of the $\tilde{X}\,^2A'$ ground and $\tilde{A}\,^2A''$ excited electronic states of the formic acid cation, are of importance for analysis of the VUV absorption spectra, in particular concerning Rydberg series converging to these ion states [2]. Earlier He I PES of HCOOH have been recorded by Brundle et al. [3] at a resolution of the order of 35 meV, Turner et al. [4] and Thomas [5] (stated resolution ≈ 40 meV). Watanabe et al. [6] investigated the He I PES of the four isotopomers HCOOH, DCOOD, HCOOD and DCOOH at a stated resolution of 28 meV at the Xe $^2P_{3/2}$ peak at 12.127 eV. Cannington

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and Ham have measured the relative intensities of corresponding bands in He I (40 meV resolution) and He II (100 meV resolution) PES of formic acid [7]. The energy resolution in our He I PES study of HCOOH and DCOOD is 15 meV. The analysis bears principally on the vibrational structure in bands I and II.

2. Experimental

The experimental set-up has been described in detail recently [8]. Here, we give only a brief description of the experimental technique and procedure. He I photons ($E = 21.21$ eV), produced in a microwave discharge, are guided through a glass capillary into the ionization region of a tandem electron spectrometer working at constant energy resolution throughout the whole energy regime under study. The pressure of the target gas in the ionization region is of the order of a few 10^{-3} mbar. HCOOH and DCOOD were from Aldrich at the highest available purity. The degree of deuteration of DCOOD is specified to be at least 99%.

The energy calibration of the PES is obtained by measuring the PES of a mixture of rare gases X (X = Ar, Kr, Xe). The well-known respective ionization energies IE to form $X^+(^2P_{3/2})$ and $X^+(^2P_{1/2})$ are used to calibrate the PES energy scale. The rare gas IEs are further used to carry out a linear regression, giving the absolute precision of the energy scale, which is ±2 meV. All spectra shown in the figures are unsmoothed. The location of peak positions was assisted by smoothed spectra.

3. Results and discussion

Our PES of HCOOH and DCOOD are shown in Figs. 1 and 2. Visual comparison of published PES of formic acid [3–6] shows that our resolution is considerably better than previous studies since bands are resolved in our spectra which are not seen or are inflexions in published spectra. Comparison with the PES of HCOOH monomers and dimers measured by Thomas [5] showed that our spectra contained no dimer features, which is as would be expected at the low pressures and the temperature of our formic acid target gas.

3.1. Electron configurations, geometrical structures and vibrational modes of neutral and ionic formic acid

Before entering on a detailed discussion of the PES of formic acid it is necessary to examine the electron configurations, geometrical structures and vibrational modes of HCOOH and $HCOOH^+$ in the relevant electronic states, beginning with the neutral ground state. This will enable us to predict

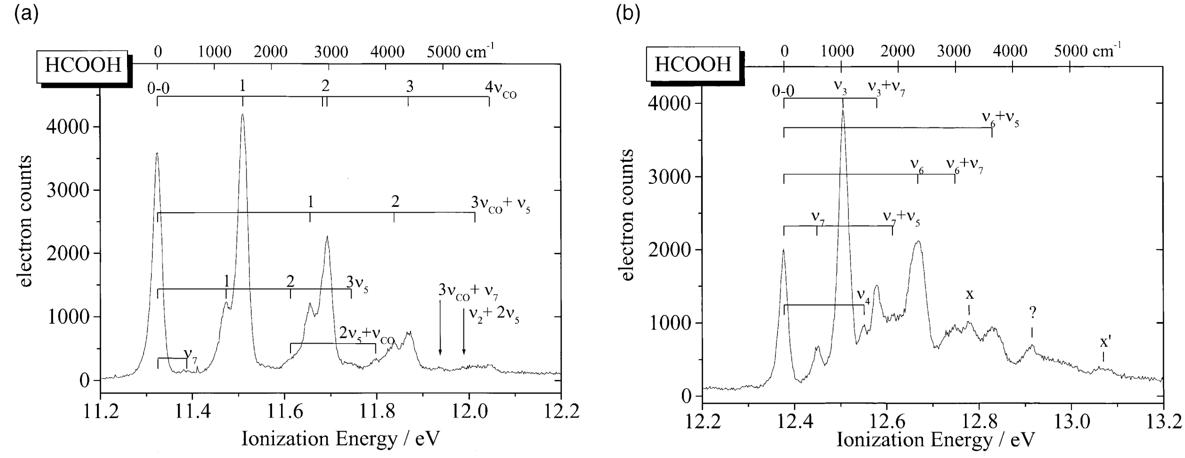

Fig. 1. He I photoelectron spectrum of HCOOH: (a) band I and (b) band II.

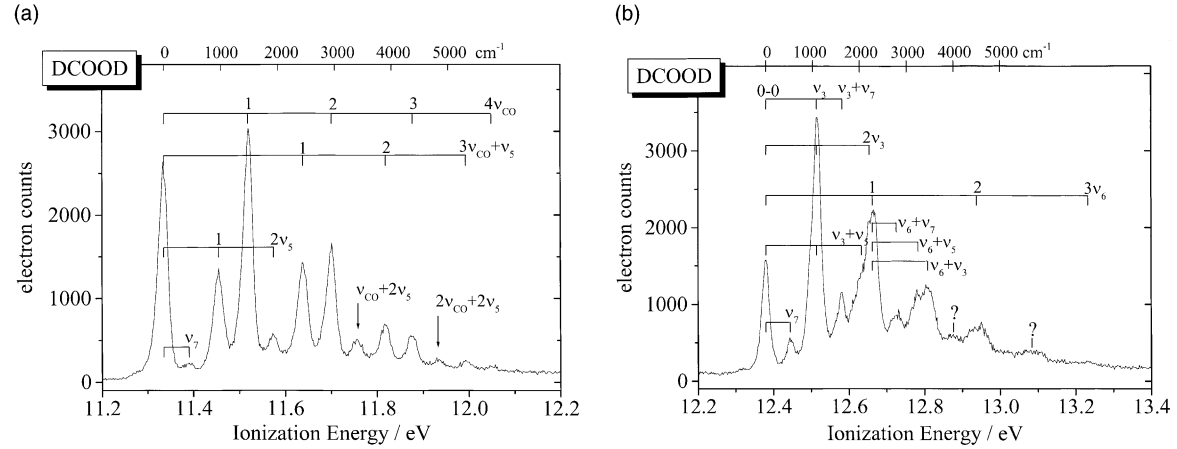

Fig. 2. He I photoelectron spectrum of DCOOD: (a) band I and (b) band II.

the structural changes expected on ionization and thus help in assignment of observed PES.

The ground state of neutral formic acid is planar and belongs to the C_s symmetry group, according to the geometrical structure determined by microwave spectroscopy of a large set of formic acid isotopomers. Its structure depicted in Fig. 3, from the work of Davis et al. [9], corresponds to the lowest energy isomer, of *cis* (or *anti*) configuration. The *trans* (or *syn*) isomer of HCOOH lies about 90 meV above the *cis* isomer according to gas phase infrared spectroscopic studies [10] and more precisely at 169 meV, from the assignment and relative intensities of weak lines in the microwave spectrum [11,12].

The electron configuration of HCOOH, in the usually accepted Hartree–Fock approximation canonical orbital energy order [3], is as follows:

$$\ldots(8a')^2(1a'')^2(9a')^2(2a'')^2(10a')^2, 1\,^1A'$$

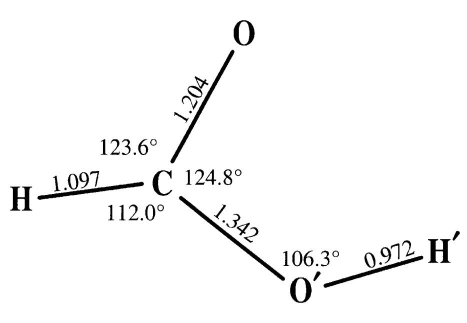

Fig. 3. Experimentally determined structure of the ground state of HCOOH [9]. Internuclear distances in Å units.

According to the ab initio calculations of Demoulin [13], supplemented by those of Itawa and Morokuma [14] and the (unpublished) SCF MO calculations of Tabayashi et al. [15], the bonding characters of the various molecular orbitals can be considered as follows:

- 10a′ is mainly non-bonding n_O on the O atom lone pair of the carbonyl group,
- 2a″ is $\pi_{C=O}(\pi_2)$ mixed with n_{OH}, and is mainly localized on the O atom of OH,
- 9a′ is σ_{CO} within the O–C–O framework, mixed with n_{OH}, bonding in OH,
- 1a″ is $\pi_{CO}(\pi_1)$ mixed with n_{OH},
- 8a′ is σ_{OH}.

The two lowest unoccupied molecular orbitals are:

- 3a″, which is a π^* M.O.
- 11a′ which is the antibonding in OH analogue of orbital 9a′.

Table 1 gives the vibrational modes and frequencies of four isotopomers of neutral formic acid in its ground state, based on the IR and Raman spectra of several groups [10,16–18]. This table also indicates the mode type and the isotopic frequency ratios DCOOD/HCOOH. These data show that the mode frequency dependence of the

Table 1
Vibrational modes and frequencies of ground state HCOOH and its isotopomers[a]

Symmetry	Mode number	Mode type	HCOOH (ν/cm^{-1})	DCOOD (ν/cm^{-1})	DCOOH (ν/cm^{-1})	HCOOD (ν/cm^{-1})
a′	ν_1	ν(OH)	3569	2632 (0.74)[b]	3570	2632
a′	ν_2	ν(CH)	2942	2232 (0.76)	2220	2948
a′	ν_3	ν(C=O)	1777	1742 (0.98)	1756	1772
a′	ν_4	δ(HCO)	1381	945 (0.68)	970	1360[c]
a′	ν_5	δ(H′O′C)	1223	1040 (0.85)	1220[c]	990
a′	ν_6	ν(C–O)	1104	1171 (1.06)	1143	1178
a′	ν_7	δ(OCO′)	625	556 (0.89)	629	541
a″	ν_8	δ(CH)	1033	873 (0.85)	867[d]	1038[d]
a″	ν_9	δ(OH)	642	489 (0.76)	629	512

[a] From IR and Raman data [10,16–18].

[b] Values in parentheses = ν(DCOOD)/ν(HCOOH).

[c] Values calculated by the product rule [16].

[d] Values calculated by a normal co-ordinate treatment [10].

hydrogen isotope is most marked for the in-plane vibrations ν_1, ν_2, ν_4 and ν_5, as well as the out-of-plane vibrations ν_8 and ν_9 (a torsional vibration), whereas there is relatively little change with isotope for the two carbon–oxygen stretch vibrations ν_3 and ν_6. The OCO deformation vibration, ν_7, is also somewhat sensitive to the presence of a hydrogen or deuterium atom in the hydroxyl bond.

Although the force field will change on ionization, we will assume that the mode frequency dependence on isotope will be similar in the ground state and first excited states of the ion, which remains planar in both states (see below). This will assist us in assignment of the vibrational structures in the PES.

3.2. Analysis of the first photoelectron band of formic acid (PES band I)

3.2.1. Structural changes on ionization to the $\tilde{X}\,^2A'$ state

We first discuss the electronic structure of the formic acid ion ground state and the geometrical and mode frequency changes that are expected to occur on ionization from the neutral ground state. The ground state of the ion has the electron configuration:

$$\ldots(8\mathrm{a}')^2(1\mathrm{a}'')^2(9\mathrm{a}')^2(2\mathrm{a}'')^2(10\mathrm{a}'),\ \tilde{\mathrm{X}}\,^2\mathrm{A}'.$$

Bell et al. [19] consider the ion ground state to be planar and this is corroborated by the ab initio calculations of Uggerud et al. [20].

In Tables 2 and 3 we compare the geometric parameters of the ground and first excited ion states with those of the neutral ground state whose structure is given in Fig. 3. The HCOOH ground state experimental data are from the determination of Davis et al. [9] and are compared in Tables 2 and 3 with the calculated values determined by Nguyen et al. [21,22], who used the UHF/6-21G** method, and by Takeshita [23] using Roothaan's restricted Hartree–Fock (RHF) method to find the optimum molecular structure. Both Nguyen et al. and Takeshita also calculated the geometrical parameters of the formic acid ion ground state $\tilde{\mathrm{X}}\,^2\mathrm{A}'$ and the first excited $\tilde{\mathrm{A}}\,^2\mathrm{A}''$ and these are reported in Tables 2 and 3 in the form of percentage change from the calculated parameter values in the neutral ground state.

The HCOOH ground state geometry calculated by Nguyen et al. and by Takeshita are very close to the experimental values, the biggest differences concern the carbon–oxygen bond distances which, as will be seen, are sensitive parameters in our analysis and discussion. In this analysis we consider structural changes between theoretically calculated geometries of the HCOOH and HCOOH$^+$ states. There is excellent agreement between the percentage changes in the geometrical parameters calculated by Nguyen et al. [21,22] and Takeshita [23] (Tables 2 and 3). These changes help to orient us as to the implications concerning the excitation of particular vibrational modes in the ground (Table 2) or first excited (Table 3) state of the

Table 2
Structural parameter values of ground state of neutral HCOOH $\tilde{\mathrm{X}}\,{}^1\mathrm{A}'$ and of ion HCOOH^+ $\tilde{\mathrm{X}}\,{}^2\mathrm{A}'$

Parameter	HCOOH $\tilde{\mathrm{X}}\,{}^1\mathrm{A}'$[a]	HCOOH $\tilde{\mathrm{X}}\,{}^1\mathrm{A}'$[b]	HCOOH $\tilde{\mathrm{X}}\,{}^1\mathrm{A}'$[c]	HCOOH cation $\tilde{\mathrm{X}}\,{}^2\mathrm{A}'$ % change[b]	HCOOH cation $\tilde{\mathrm{X}}\,{}^2\mathrm{A}'$ % change[c]	Frequency implications $\tilde{\mathrm{X}}\,{}^2\mathrm{A}' \leftarrow \tilde{\mathrm{X}}\,{}^1\mathrm{A}'$
r(C=O)/Å	1.204	1.182	1.179	+6.6	+4.4	$\nu'_3 < \nu''_3$
r(C–O′)/Å	1.342	1.322	1.321	−5.82	−5.90	$\nu'_6 > \nu''_6$
r(C–H)/Å	1.097	1.085	1.094	−0.02	−0.03	$\nu'_2 \geqslant \nu''_2$
r(O′–H′)/Å	0.972	0.949	0.952	+1.16	+1.26	$\nu'_1 < \nu''_1$
HCO angle	123.6°	124.6°	124.8°	−6.26	−5.65	$\nu'_4 > \nu''_4$
H′O′C angle	106.3°	108.9°	108.4°	+8.10	+7.52	$\nu'_9 < \nu''_9$, $\nu'_5 < \nu''_5$
HCO′ angle	112.0°	110.5°	110.3°	+8.14	+6.72	$\nu'_8 < \nu''_8$
OCO′ angle	124.8°	124.9°	124.9°	−0.97	−0.85	$\nu'_7 \geqslant \nu''_7$

[a] Experimental structure [9].
[b] Calculated structures [21].
[c] Calculated structures [23].

Table 3
Structural parameter values of ground state neutral HCOOH $\tilde{\mathrm{X}}\,{}^1\mathrm{A}'$ and of ion first excited state HCOOH^+ $\tilde{\mathrm{A}}\,{}^2\mathrm{A}''$

Parameter	HCOOH $\tilde{\mathrm{X}}\,{}^1\mathrm{A}'$ state[a]	HCOOH $\tilde{\mathrm{X}}\,{}^1\mathrm{A}'$ state[b]	HCOOH $\tilde{\mathrm{X}}\,{}^1\mathrm{A}'$ state[c]	HCOOH cation $\tilde{\mathrm{A}}\,{}^2\mathrm{A}''$ state % change[b]	HCOOH cation $\tilde{\mathrm{A}}\,{}^2\mathrm{A}''$ state % change[c]	Frequency implications $\tilde{\mathrm{A}}\,{}^2\mathrm{A}'' \leftarrow \tilde{\mathrm{X}}\,{}^1\mathrm{A}'$
r(C=O)/Å	1.204	1.182	1.179	+11.84	+12.55	$\nu'_3 < \nu''_3$
r(C–O′)/Å	1.342	1.322	1.321	−5.75	−7.34	$\nu'_6 > \nu''_6$
r(C–H)/Å	1.097	1.085	1.094	−0.55	−0.55	$\nu'_2 \geqslant \nu''_2$
r(O′–H′)/Å	0.972	0.949	0.952	+1.90	+1.79	$\nu'_1 < \nu''_1$
HCO angle	123.6°	124.6°	124.8°	−1.44	−2.73	$\nu'_4 > \nu''_4$
H′O′C angle	106.3°	108.9°	108.4°	+6.98	+6.70	$\nu'_9 < \nu''_9$, $\nu'_5 < \nu''_5$
HCO′ angle	112.0°	110.5°	110.3°	+4.91	+5.61	$\nu'_8 < \nu''_8$
OCO′ angle	124.8°	124.9°	124.9°	−4.16	−3.64	$\nu'_7 \geqslant \nu''_7$

[a] Experimental structure [9].
[b] Calculated structures [21,22].
[c] Calculated structures [23].

formic acid ion, as given in the last column of Tables 2 and 3. Takeshita reports calculations of the vibrational frequencies of the totally symmetrical modes of the neutral ground state and the cation $\tilde{\mathrm{X}}\,{}^2\mathrm{A}'$ and $\tilde{\mathrm{A}}\,{}^2\mathrm{A}''$ states. The sense of the calculated frequency changes are in good agreement with the implications given in Tables 2 and 3, except for ν_7 in both states, where Takeshita's predictions are $\nu'_7 \leqslant \nu''_7$, and for ν_6 in the $\tilde{\mathrm{A}}\,{}^2\mathrm{A}''$ state where his predictions are $\nu'_6 \leqslant \nu''_6$, in startling contradiction to the reverse order which is strongly implied by the considerable shortening of r(C–O′) calculated for ionization to the $\tilde{\mathrm{A}}\,{}^2\mathrm{A}''$ state. The calculated order implies considerable contributions from other parameter changes in the potential energy distribution for the modes ν_6, as determined by Takeshita for the neutral and ion states [23]. However, the experimental values of ν_6 for the neutral ground state of the four isotopomers (Table 1) indicate that the potential distributions are in considerable error, since Takeshita calculated a change of ν_6 of −16.9% on going from HCOOH to DCOOD, whereas experimentally the change is +6.07% (Table 1).

When there are implications of notable changes in the vibrational mode frequencies on ionization we expect excitation of progressions in these modes, whose intensities are modulated by the appropriate Franck–Condon factors. As will be seen below, comparison with experimental observation determines the degree of validity of this approach and of the calculations on the formic acid ion states.

The first ionization energy of formic acid (HCOOH), determined from Rydberg band analysis of absorption spectra, is reported as 11.329 ± 0.002 eV [19]. The first excited state of the ion has a reported appearance energy of 12.37 eV [3]. Our observed PES values for these two ionization energies are 11.3246 and 12.3783 eV respectively (Table 4, energy scale precision ±2 meV), in excellent agreement with the literature values. In fact, our values for the first and second ionization energies of DCOOD, 11.3353 and 12.3801 eV respectively (Table 5), and the second ionization energies of HCOOH are the most accurate yet reported.

Table 4
Assignment of photoelectron spectrum bands I and II of HCOOH

Band no.	E/eV	E/cm^{-1}	$\Delta\nu$/cm^{-1}	Assignment	
PES band I					
1	11.3246	91 339	0	0–0	
2	11.3879	91 849	510	ν_7	
3	11.473	92 535	1196	ν_5	
4	11.51	92 834	1495	ν_{CO}	
5	11.6131	93 665	2326	$2\nu_5$	
6	11.6557	94 009	2670	$\nu_{CO} + \nu_5$	
7	11.683	94 229	2890	$2\nu_{CO}^{*}$	
8	11.6926	94 307	2968	$2\nu_{CO}$	
9	11.745	94 727	3388	$3\nu_5$	
10	11.798	95 157	3818	$\nu_{CO} + 2\nu_5$	
11	11.838	95 479	4140	$2\nu_{CO} + \nu_5$	
12	11.8693	95 732	4393	$3\nu_{CO}$	
13	11.937	96 278	4939	$3\nu_{CO} + \nu_7$	
14	11.9882	96 691	5352	$\nu_2 + 2\nu_5$	
15	12.0126	96 888	5549	$3\nu_{CO} + \nu_5$	
16	12.0452	97 151	5812	$4\nu_{CO}$	
PES band II				Assignment	
				A	B
17	12.3783	99 837	0	0–0	0–0
18	12.4494	100 411	574	ν_7	ν_7
19	12.5059	100 866	1029	ν_3	ν_3
20	12.5516	101 235	1398	ν_4	ν_4
21	12.5794	101 459	1622	ν_6	$\nu_3 + \nu_7$
22	12.6136	101 735	1898	?	$\nu_5 + \nu_7$
23	12.6688	102 180	2343	?	ν_6
24	12.7483	102 821	2984	?	$\nu_6 + \nu_7$
25	12.779	103 069	3232	$2\nu_6$	x (see text)
26	12.8294	103 476	3639	?	$\nu_6 + \nu_5$
27	12.9151	104 167	4330	?	?
28	13.07	105 416	5579	?	$x + \nu_6$

Table 5
Assignment of photoelectron spectrum bands I and II of DCOOD

Band no.	E/eV	E/cm^{-1}	$\Delta\nu$/cm^{-1}	Assignment	
PES band I					
1	11.3353	91 425	0	0–0	
2	11.3907	91 872	447	ν_7	
3	11.445	92 390	965	ν_5	
4	11.5178	92 897	1472	ν_{CO}	
5	11.5744	93 353	1928	$2\nu_5$	
6	11.6381	93 867	2442	$\nu_{CO} + \nu_5$	
7	11.7006	94 371	2946	$2\nu_{CO}$	
8	11.7582	94 386	3411	$\nu_{CO} + 2\nu_5$	
9	11.8187	95 324	3899	$2\nu_{CO} + \nu_5$	
10	11.8771	95 795	4370	$3\nu_{CO}$	
11	11.9336	96 250	4826	$2\nu_{CO} + 2\nu_5$	
12	11.9931	96 730	5305	$3\nu_{CO} + \nu_5$	
13	12.0487	97 179	5756	$4\nu_{CO}$	
PES band II				Assignment	
				A	B
14	12.3801	99 852	0	0–0	0–0
15	12.4447	100 373	521	ν_7	ν_7
16	12.5147	100 937	1085	ν_3	ν_3
17	12.5815	101 476	1624	ν_6	$\nu_3 + \nu_7$
18	12.611	101 710	1858	?	?
19	12.633	101 891	2039	?	$\nu_3 + \nu_5$
20	12.654	102 061	2209	$2\nu_3$	$2\nu_3$
21	12.662	102 125	2273	?	ν_6
22	12.7257	102 639	2787	?	$\nu_6 + \nu_7$
23	12.7829	103 100	3248	$2\nu_6$	$\nu_6 + \nu_5$
24	12.8082	103 305	3453	?	$\nu_3 + \nu_6$
25	12.8767	103 857	4005	?	?
26	12.9379	104 351	4499	?	$2\nu_6$
27	13.0837	105 527	5675	?	?
28	13.2329	106 730	6878	?	$3\nu_6$

In the following discussion and analysis of the PES of formic acid we consider in parallel the observations on HCOOH and DCOOD, using the comparison between the PES features of these two isotopomers to strengthen and validate assignments. With this objective, data from the less well-resolved spectra of Watanabe et al. on HCOOD and DCOOH [6] will also be used on occasion. The band energy data in Tables 4 and 5 are given in eV and in cm^{-1}. The reproducibility of the measurements, carried out after smoothing by averaging of five adjacent points, is better than 5 cm^{-1}. However, many band profiles are such that they may represent overlapping features, giving rise, in some cases, to asymmetric band shapes. We recall that the energy resolution is of the order of 120 cm^{-1}. Thus the accuracy of vibrational frequencies derived from measurements of particular shoulders or of broad weak bands is estimated to be no better than ±20 cm^{-1}. Fortunately, the existence of combination and harmonic bands enables more accurate values to be obtained in some cases.

3.2.2. *Carbon–oxygen stretch vibrations*

In our analysis of the first PES band in HCOOH (Table 4, band I) we first considered whether the bands at 1495 and 1196 cm^{-1} from the origin are respectively ν_3 and ν_6 or ν_6 and ν_3. In the neutral ground state these two modes correspond essentially to C=O and C–O stretching vibrations respectively, with $\nu_3 > \nu_6$. From Table 2 we expect ν_3 to diminish on ionization and ν_6 to increase. In fact, the calculated carbon–oxygen bond lengths are such that we might expect the ν_6 frequency to be greater than ν_3 in the ion ground state.

However, although the DCOOD PES band I (Fig. 2, Table 5) has a strong band at 1472 cm^{-1}, similar in frequency and in intensity to the HCOOH band at 1495 cm^{-1}, there is no DCOOD feature corresponding to the 1196 cm^{-1} band of HCOOH. From the neutral ground state isotopic frequencies we expect only a small deuterium isotope shift for the carbon–oxygen stretch vibrations. The DCOOD band at 965 cm^{-1} would correspond to a large isotope shift with respect to HCOOH and it is thus not expected to be a carbon–oxygen stretch vibration. Its assignment, as well as that of the HCOOH 1196 cm^{-1} band is discussed later. Thus it is clear that the 1495 cm^{-1} band in HCOOH and 1472 cm^{-1} band in DCOOD are carbon–oxygen stretch vibrations of the same mode. Whether it is ν_3 or ν_6 requires further consideration.

A zero-order estimation of the ν_3 and ν_6 frequencies in the ion states can be made on the basis of a plot of carbon–oxygen stretch mode frequencies and carbon–oxygen bond lengths in neutral HCOOH and CO. The basic data comes from experimental values pertaining to the ground and excited electronic states of HCOOH [9,10,16–18,24] and CO [25]. Fig. 4 shows this data from which we interpolate to obtain the following carbon–oxygen stretch frequencies at the various calculated bond lengths: HCOOH$^+$ $\tilde{X}$ state: ≈1590 cm^{-1} (r(CO) = 1.257 Å), ≈1660 cm^{-1} (r(CO) = 1.243 Å). In the ion ground state it is thus probable that the ν_3 and ν_6 are close in value, so that the 1495 cm^{-1} band in HCOOH and 1472 cm^{-1} band in DCOOD, which have FWHM ≈200 and 180 cm^{-1}, respectively, may each be the superposition of two bands, corresponding to excitation of the ν_3 and ν_6 modes. The profile of the 1472 cm^{-1} band in DCOOD shows some indication of underlying multiple features. Henceforward we assign such bands involving these two vibrational modes, which we have inferred as being quasi-degenerate in frequency, with the notation ν_{CO}.

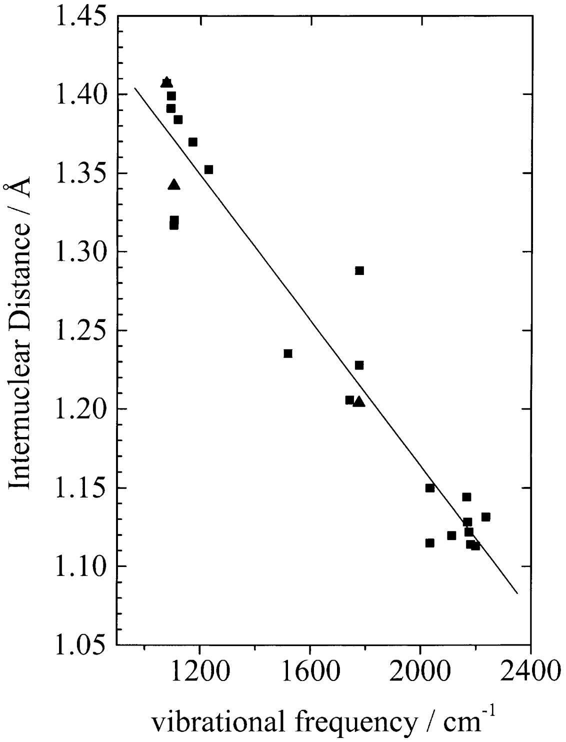

Fig. 4. Carbon–oxygen vibrational frequency ν_{CO} as a function of internuclear distance r_{CO}: triangles = data from HCOOH [9,10,16–18,25] and squares = diatomic CO [26], see text.

We consider now progressions in ν_{CO}. The band at 2890 cm^{-1} is assigned as one component of the couple $\{2\nu_3; 2\nu_6\}$, the other component being the band at 2968 cm^{-1} which we conventionally assign as $2\nu_{\mathrm{CO}}$. The inference here is that the single quanta bands ν_3 and ν_6 are unresolved at 1495 cm^{-1} but that the two quanta bands begin to be resolved. From this we estimate that $|\nu_3 - \nu_6| \approx (2968 - 2890)/2 = 39\ \mathrm{cm}^{-1}$. We denote the 2890 cm^{-1} band as $2\nu^*_{\mathrm{CO}}$, thus not differentiating between the various two quanta combinations between ν_3 and ν_6. The corresponding isotopic feature is not resolved in DCOOD, which indicates that $|\nu_3 - \nu_6|$ is smaller in the $\widetilde{\mathrm{X}}\,^2\mathrm{A}'$ state of DCOOD than in HCOOH.

It should be mentioned that the HCOOH feature at 2890 cm^{-1} is in a region where a ν_2 frequency could occur. However, excitation of ν_2, a C–H stretch vibration, is not expected to be very active; furthermore, on ionization it should increase only very slightly in frequency from the neutral ground state value 2942 cm^{-1} (Table 2), which is not the case here. We later discuss assignments of bands involving ν_2.

Higher members of the ν_{CO} progression are observed in both HCOOH and DCOOD. For HCOOH these are $3\nu_{\mathrm{CO}}$ and $4\nu_{\mathrm{CO}}$ at 4393 and 5812 cm^{-1} respectively, the successive frequency differences of the progression being 1495, 1473, 1425 and 1419 cm^{-1}. The broadness of the bands in the $3\nu_{\mathrm{CO}}$ and $4\nu_{\mathrm{CO}}$ regions is probably due to the possibility of several mode combinations, e.g. $\{2\nu_3 + \nu_6;\ \nu_3 + 2\nu_6\}$ in the $3\nu_{\mathrm{CO}}$ region, $\{n\nu_3 + m\nu_6;$ positive integers $\mathrm{n} + \mathrm{m} = 4\}$ in the $4\nu_{\mathrm{CO}}$ region.

The $3\nu_{\mathrm{CO}}$ and $4\nu_{\mathrm{CO}}$ bands of DCOOD are observed at 4370 and 5756 cm^{-1} respectively, the successive frequency differences of the progression being 1472, 1474, 1424 and 1386 cm^{-1}. The bands in the $3\nu_{\mathrm{CO}}$ and $4\nu_{\mathrm{CO}}$ regions are less broad than in HCOOH, which is in agreement with the inference above that the frequency difference $|\nu_3 - \nu_6|$ is smaller in DCOOD than in HCOOH.

We note that Takeshita [23] who used his theoretical results to analyse the HCOOH and DCOOD PES of Watanabe et al. [6], assigned the progression which we call $n\nu_{\mathrm{CO}}$, to a progression in $n\nu_3$ alone. We have given above our arguments why this is an insufficient assignment.

3.2.3. The $\delta(H'O'C)$ bending mode vibration ν_5

We next assign the 1196 cm^{-1} band of HCOOH as the H′O′C bending mode vibration ν_5. Frequencies in this range (±200 cm^{-1}) in the neutral ground state of HCOOH occur for modes 4 (1381 cm^{-1}), 5 (1223 cm^{-1}), 6 (1104 cm^{-1}) and 8 (1033 cm^{-1}). From Table 2 we see that mode 4 could be active on ionization to the ground state of HCOOH^+, so that we can consider this mode as one possible assignment of the relatively intense band at 1196 cm^{-1}. However, from Table 2, modes 5 and 6 are also expected to be vigorously excited, and mode 8 to be moderately active. We have already discussed ν_6 and shown that it appears most probably as part of the ν_{CO} band at 1495 cm^{-1}. From the isotopic frequency ratios (Table 1), mode 8 would be expected to give rise to a band at about 1010 cm^{-1} in DCOOD. There is a band at 965 cm^{-1} in DCOOD. If this were indeed the ν_8 band we would expect, from the isotope ratios in Table 1, to observe a relatively intense ν_8 band at about 965 cm^{-1} in DCOOH. Examination of the He I photoelectron spectrum of this isotopomer [6] does not reveal the existence of a band at this frequency. We can thus eliminate ν_8 as an assignment for the 1196 cm^{-1} band in HCOOH. There remain, as possible assignments, ν_4 and ν_5, the former being a δ(HOC) vibration and the latter a δ(H′O′C) vibration. From the isotope relations of Table 1 we predict ν_4 bands at about 813 cm^{-1} in DCOOD, 840 cm^{-1} in DCOOH and 1178 cm^{-1} in HCOOD and ν_5 bands at about 1015 cm^{-1} in DCOOD, 1195 cm^{-1} in DCOOH and 970 cm^{-1} in HCOOD. Features in the Watanabe et al. PES of these isotopomers [6], as well as our own spectrum of DCOOD (Fig. 2), strongly support the assignment to ν_5, although Takeshita, on the basis of his calculations, prefers ν_4 in HCOOH but ν_5 in DCOOD [23].

The band at 2326 cm^{-1} of HCOOH is assigned as $2\nu_5$. The fairly large anharmonicity of this vibration is not surprising for a deformation mode in which it is essentially the H′O′C angle which is oscillating. One more member of a ν_5 progression is assigned, a weak band $3\nu_5$ at 3388 cm^{-1}. A band at 2670 cm^{-1} is assigned to the combination $\nu_{\mathrm{CO}} + \nu_5$ (expected at $1196 + 1495 = 2692\ \mathrm{cm}^{-1}$ which is within the precision of measurement at our PES resolution).

In the DCOOD photoelectron spectrum we observe and assign bands corresponding to the above ν_5 features, as follows: 965 $\mathrm{cm}^{-1} = \nu_5$; 1928 $\mathrm{cm}^{-1} = 2\nu_5$; 2442 $\mathrm{cm}^{-1} = \nu_{\mathrm{CO}} + \nu_5$ (expected at $1472 + 965 = 2437$ cm^{-1}), in excellent isotopic agreement with the HCOOH assignments.

The HCOOH feature at 3818 cm^{-1} is assigned as $\nu_{\mathrm{CO}} + 2\nu_5$ (expected value $= 1495 + 2326 = 3821$ cm^{-1}) and the 4140 cm^{-1} band as $2\nu_{\mathrm{CO}} + \nu_5$ (expected value $= 2968 + 1196 = 4164$ cm^{-1}). These assignments are confirmed by the DCOOD feature at 3411 cm^{-1}, assigned as $\nu_{\mathrm{CO}} + 2\nu_5$ (expected value $= 1472 + 1928 = 3400$ cm^{-1}) and the 3899 cm^{-1} band as $2\nu_{\mathrm{CO}} + \nu_5$ (expected value $= 2946 + 965 = 3911$ cm^{-1}). The assignments involving ν_{CO} and ν_5 are further supported by the PES of HCOOD [6] which, as expected from Table 1, show these features at similar frequencies to those of DCOOD.

Some other combination bands involving ν_5 were assigned. In HCOOH the $3\nu_{\mathrm{CO}} + \nu_5$ band is at 5549 cm^{-1} (expected value $= 4393 + 1196 = 5589$ cm^{-1}), while in DCOOD the corresponding $3\nu_{\mathrm{CO}} + \nu_5$ band occurs at 5305 cm^{-1} (expected value $= 4370 + 965 = 5335$ cm^{-1}). A band in DCOOD at 4826 cm^{-1} is assigned as $2\nu_{\mathrm{CO}} + 2\nu_5$ (expected value $= 2946 + 1928 = 4874$ cm^{-1}). The corresponding band in HCOOH would occur within a broad, not well-resolved, high energy feature, in a region where we have assigned a band to $\nu_2 + 2\nu_5$, as discussed later.

We remark that the band progression assigned as $\nu_5 + n\nu_{\mathrm{CO}}$ in our HCOOH spectrum (Fig. 1) is assigned as $\nu_6 + n\nu_3$ by Takeshita, with no corresponding assignments in DCOOD [23].

3.2.4. The $\delta(OCO')$ bending mode vibration ν_7

We turn now to the assignment of the HCOOH band at around 510 ± 20 cm^{-1} and the corresponding DCOOD band at 447 cm^{-1}. From the order of magnitude of the observed frequencies, two assignments are possible a priori, ν_9 and/or ν_7, mode 9 being an out-of-plane motion, mode 7 an in-plane motion (Table 1). These ion state frequencies are smaller than those of the neutral ground state, in agreement with the implications given in Table 2 for ν_9 but not for ν_7. However, the ion state value for ν_7 calculated by Takeshita is less than for the neutral state [23]. Although in the potential energy distribution for ν_7, calculated by Takeshita, the OCO′ bend is of identical relative major contribution in both the neutral and ion ground states, the relative minor contribution of the H′O′C and HCO bends is very different in these two ground states and it is this that most probably leads to a smaller value of ν_7 in the ion ground state. The DCOOD/HCOOH frequency ratios R of neutral formic acid are $R(\nu_9) = 0.76$, $R(\nu_7) = 0.89$, whereas in the ion $R = 0.88$, close to the neutral value for ν_7. On this basis we assign the low-frequency bands to mode 7 rather than to the out-of-plane vibration ν_9. An attempt was made to ascertain whether there are combination bands involving ν_7. Although one can assign quite well $(n\nu_{\mathrm{CO}} + \nu_7)$ $n = 1, 2, 3$ features in DCOOD, with $\nu_7 = 447$ cm^{-1}, at respectively (expected values in parentheses) 1928 (1919) cm^{-1}, 3411 (3393) cm^{-1} and 4826 (4817) cm^{-1}, the expected intensity ratios are not observed, perhaps due to band overlap. The corresponding isotopic bands are not clearly seen in HCOOH, except for $(3\nu_{\mathrm{CO}} + \nu_7)$ at 4939 (4903) cm^{-1}. This is the only $n\nu_{\mathrm{CO}} + \nu_7$ combination band that we propose as an assignment in HCOOH.

3.2.5. Bands involving the C–H stretch vibration ν_2

There remains to discuss the weak feature at 5352 cm^{-1} in HCOOH. This could be a combination band involving ν_2 or ν_1, whose frequencies in the ion ground state we estimate to be around 2950 and 3520 cm^{-1} respectively (2240 and 2600 cm^{-1} for DCOOD). The fundamental frequency bands of ν_2, but not ν_1, could be hidden in overlapping bands in HCOOH and DCOOD PES band I. We do not see any features that could correspond to the ν_1 fundamental frequencies. However, from Table 2 we do not expect ν_1 or ν_2 to be very active. Nevertheless, we assign the 5352 cm^{-1} feature to $\nu_2 + 2\nu_5$, which gives $\nu_2 = 3026$ cm^{-1}. In DCOOD there is a shoulder at 4232 cm^{-1}, which we assign as the corresponding combination band in this isotopomer, giving $\nu_2 = 2304$ cm^{-1} for DCOOD. These frequencies are in satisfactory agreement with our estimated values. The assignments led us to search for $\nu_2 + \nu_5$ bands at 4222 cm^{-1} (HCOOH) and 3269 cm^{-1} (DCOOD) but these would occur within the profile of stronger bands.

3.3. Analysis of the second photoelectron band of formic acid (PES band II)

3.3.1. Structural changes on ionization to the $\tilde{A}^2A''$ state

The first excited ion state, at 12.3783 eV, of configuration

$$\ldots(8a')^2(1a'')^2(9a')^2(2a'')(10a')^2,\ \tilde{A}^2A'',$$

is also planar, according to theoretical calculations [20,22,23].

In Table 3 are given the percentage changes in the structural parameters on ionization to the $\tilde{A}^2A''$ state. These indicate that on removal of the 2a″ electron there will be an increase in the C=O bond length, more important than for the ion ground state, a decrease in the C–O bond length and notable increases in the H′O′C and HCO′ angles, as well as a decrease in the OCO′ angle (cf. Fig. 3). We therefore expect to see a more substantial decrease in ν_3(C=O) than for the ion ground state, and a greater increase in ν_6(C–O) with respect to the ion ground state. In addition, excitation of modes that involve the bond angles could occur, i.e. ν_5, ν_7, ν_8 and ν_9.

We note that the simulations by Takeshita of the PES spectrum in the $\tilde{A}^2A''$ state region of the ion completely fail to reproduce the experimental spectrum of either HCOOH or DCOOD (Fig. 3 of Ref. [23]). In the following discussion we therefore find it not necessary to compare our analyses of the PES band II with those of Takeshita.

3.3.2. Two possible assignments of the carbon–oxygen stretch vibrations

Assignment A: From the correlation between carbon–oxygen stretch mode frequencies and bondlengths described previously (Fig. 4) we estimate the following vibrational frequency values for the two CO stretch vibrations in the $\tilde{A}^2A''$ state of $HCOOH^+$: $\nu_3 \approx 1300$ cm^{-1}, $\nu_6 \approx 1740$ cm^{-1}. The principal vibrational band in the PES band II of HCOOH is at 1029 cm^{-1} (Fig. 1, Table 4) and we assign this to ν_3. There is a weaker band at 1622 cm^{-1} which we attribute to ν_6 in the first instance. Similar bands occur in the DCOOD PES at 1085 and 1624 cm^{-1} respectively (Fig. 2, Table 5). It is a little surprising that ν_3 (DCOOD) > ν_3 (HCOOH). However, examination of band II in the isotopomer PES of Watanabe et al. [6] shows that this is also true for DCOOH but not for HCOOD, which indicates that there is some interaction between the CH stretch and C–O motions. On deuteration, the resulting CD vibrational frequencies are closer to the C–O values than are the CH frequencies (Table 1), so that an increased interaction becomes possible with deuteration, which we postulate as leading to ν_3 (DCOOD) > ν_3 (HCOOH).

Our CO stretch assignments can be compared with the vibrational data of the $\tilde{A}^2A''$ state that can be extracted from the PES of Brundle et al. [3] and of Watanabe et al. [6], as well as from the threshold photoelectron spectra (TPES) of Ruscic et al. [26]. Brundle et al. [3] give as principal vibration for HCOOH $\nu = 1120 \pm 30$ cm^{-1}, without specifying to which mode this belongs, while Watanabe et al. [6] propose the following assignments, $\nu_3(\mathrm{C{=}O}) = 2339$ cm^{-1}, $\nu_6(\mathrm{C{-}O}) = 1053$ cm^{-1}. The value $\nu_3(\mathrm{C{=}O}) = 2339$ cm^{-1} is in flagrant disagreement with our expectations outlined in Table 2 where we predict a large *decrease* in ν_3(C=O) with respect to the neutral ground state frequency $\nu_3(\mathrm{C{=}O}) = 1777$ cm^{-1} (but see later).

The TPES of Ruscic et al. [26] in the region of the first excited state of the $HCOOH^+$ and $DCOOD^+$ ions are better resolved (18 meV) than the PES of Brundle et al. [3] and of Watanabe et al. [6] (≈35 meV). This TPES spectrum is analyzed in Appendix, from which we extract the following vibrational frequencies of the $\tilde{A}^2A''$ state of $HCOOH^+$: 1017 (1077 for $DCOOD^+$) cm^{-1} and 1620 cm^{-1}, which are very close to the values we obtain from our PES of HCOOH (and DCOOD) and assign to ν_3 and ν_6, respectively, in band II assignment A of Tables 4 and 5.

We observe also possible $2\nu_6$ bands at 3232 cm^{-1} (HCOOH), 3248 cm^{-1} (DCOOD). Higher members of a ν_6 progression, expected at 4800–4900 cm^{-1} are not resolved in this broad weak features region of both spectra.

However, the strong HCOOH band at 2343 cm^{-1} is difficult to assign unequivocally on the basis of the carbon–oxygen stretch vibration assignments of the $\tilde{A}^2A''$ state given above. This band is broad, with obvious multiple unresolved features. There is a suspicion of shoulders at 2220 and 2145 cm^{-1}. The corresponding band in DCOOD, at 2273 cm^{-1}, is also broad, with shoulders at 2209, 2039, 1858 cm^{-1}. At this level of spectral resolution it was not possible to assign the 1858 cm^{-1} shoulder (see later for assignments of the 2209 and 2039 cm^{-1} features, Table 5, band II, assignment B).

A possible assignment of the HCOOH 2343 cm^{-1} and DCOOD 2273 cm^{-1} bands is to $\nu_3 + \nu_5$, where $\nu_5 = 1314$ cm^{-1} (HCOOH), 1188 cm^{-1} (DCOOD). However, we must abandon this approach since these ν_5 frequencies are greater than those of the neutral molecule, 1223 cm^{-1} (HCOOH) and 1040 cm^{-1} (DCOOD) whereas, from the increase in the H′O′C angle (Tables 2 and 3), we expect the ν_5 frequency to be smaller in the ion states, as is indeed found for the $\widetilde{X}\,^2A'$ state of the ion (Tables 4 and 5).

Assignment B: The considerable difficulty that we had in assigning the HCOOH 2343 cm^{-1} and DCOOD 2273 cm^{-1} bands caused us to reconsider the suggestion of Watanabe et al. [6] that his 2369 (our 2343) cm^{-1} band be assigned to a CO vibration. In their case they assigned this frequency to ν_3 but here we consider rather ν_6, on the basis of Table 3. Bands of similar intensity in this frequency region were reported by Watanabe et al. [6] for the four isotopomers: 2339 cm^{-1} (HCOOH), 2283 cm^{-1} (DCOOD), 2339 cm^{-1} (DCOOH), 2329 cm^{-1} (HCOOD) [6]. We first of all note that the frequencies of these bands are of the same order of magnitude as that of the ground state of the CO$^+$ ion, which is close to 2200 cm^{-1} [25], so that it is not impossible for the ν_6 CO stretch frequency in formic acid to be of this order of magnitude if the positive charge is associated with a CO group. It is of interest that in earlier calculations, Peyerimhoff and Buenker [27] stress that the 2a″ molecular orbital will be strongly mixed with the 3a″(π_3^*) M.O., because the charge distributions of both have their maxima above and below the molecular plane in roughly the same region of space. This is expected to lead to a significant oxygen to carbon charge transfer. However, if the HCOOH 2343 cm^{-1} and DCOOD 2273 cm^{-1} bands were indeed ν_6, one should also observe fairly intense $2\nu_6$ harmonic bands. These are expected at about 4500–4700 cm^{-1} in HCOOH and at about 4400–4600 cm^{-1} in DCOOD. There is a very broad weak PES signal in the 4500–4700 cm^{-1} region in HCOOH and a fairly intense suitable feature in DCOOD, at $2\nu_6 = 4499$ cm^{-1}. The DCOOD band at 6878 cm^{-1} can be assigned as $3\nu_6$ (expected value 6819 cm^{-1}.

3.3.3. Bending vibrational modes

The low-frequency bands at 574 cm^{-1} (HCOOH) and 521 cm^{-1} (DCOOD) have a ratio $R = \nu(\mathrm{DCOOD})/\nu(\mathrm{HCOOH}) = 0.91$, close to the neutral ratio $R(\nu_7) = 0.89$, so that it is reasonable to assign them to ν_7. There is greater activity of this mode than in the ion ground state. Watanabe et al. [6] report very weak bands in HCOOH (DCOOD) at 544 (518) cm^{-1} and 631 (534) cm^{-1}. We only observe one band in this spectral region for HCOOH and DCOOD, but the asymmetry of this feature in both spectra may indicate an unresolved second component. This higher frequency component could correspond to ν_9. Only one feature is observed in this region in the threshold PES of Ruscic et al. [26] at 602 (519) cm^{-1}.

The weak but clear band at 1398 cm^{-1} in HCOOH is assigned to ν_4. This assignment leads us to expect the corresponding band in DCOOD to occur at about 950 cm^{-1}, according to the isotopic ratios given in Table 1. This feature would lie, unresolved, in the low-frequency part of the strong 1085 cm^{-1} band profile.

3.3.4. Combination bands

On adopting for ν_6 the values 2343 cm^{-1} (HCOOH) and 2273 cm^{-1} (DCOOD), we can reassign the bands previously indicated as involving this vibrational mode in assignment A of Tables 4 and 5. Thus we can re-assign the HCOOH band at 1622 cm^{-1} to $\nu_3 + \nu_7$ (expected value $= 1029 + 573 = 1602$ cm^{-1}) and the DCOOD 1624 cm^{-1} band as $\nu_3 + \nu_7$ (expected value $= 1085 + 521 = 1606$ cm^{-1}). The DCOOD band at 3453 cm^{-1} is possibly $\nu_3 + \nu_6$ (expected value $= 1085 + 2273 = 3358$ cm^{-1}). These re-assignments are given in band II assignment B of Tables 4 and 5.

It also becomes possible to assign several other bands involving ν_6. DCOOD 2787 cm^{-1} $= \nu_6 + \nu_7$ (expectation $= 2273 + 521 = 2794$ cm^{-1}).

HCOOH 2984 $\mathrm{cm}^{-1} = \nu_6 + \nu_7$ (expectation $= 2343 + 574 = 2917\ \mathrm{cm}^{-1}$), broad band (Fig. 1). DCOOD 3248 $\mathrm{cm}^{-1} = \nu_6 + \nu_5$ (expectation $= 2273 + 954 = 3227\ \mathrm{cm}^{-1}$), from which another value $\nu_5 = 975\ \mathrm{cm}^{-1}$, can be determined. The corresponding HCOOH band could be the broad feature peaking at 3639 cm^{-1}, giving ν_5 (HCOOH) $= 1296\ \mathrm{cm}^{-1}$, which is rather higher than the value, 1150 cm^{-1}, expected from the isotopic ratio in Table 1. However, we have assigned the HCOOH minor feature at 1898 cm^{-1} as $\nu_7 + \nu_5$, from which we deduce a value $\nu_5 = 1324\ \mathrm{cm}^{-1}$, close to $\nu_5(\mathrm{HCOOH}) = 1296\ \mathrm{cm}^{-1}$ determined above.

In DCOOD we have assigned the 2039 cm^{-1} band to the combination band $\nu_3 + \nu_5$. Examination of the Watanabe et al. PES of the four formic acid isotopomers [6] shows that there is a "2039 cm^{-1}" feature in the HCOOD band II but not in DCOOH. This is as expected for the isotopic behavior of ν_3 and ν_5 (Table 1), thus confirming the $\nu_3 + \nu_5$ assignment. From this we deduce $\nu_5(\mathrm{DCOOD}) = 954\ \mathrm{cm}^{-1}$, which is close to the value $\nu_5 = 975\ \mathrm{cm}^{-1}$ evaluated above. The corresponding ion $\tilde{\mathrm{A}}\,^2\mathrm{A}''$ state vibronic band in the PES of HCOOH is expected to occur at about $1029 + 1296 = 2325\ \mathrm{cm}^{-1}$. This would be hidden within the somewhat broad $\nu_3 = 2343\ \mathrm{cm}^{-1}$ band (Fig. 1).

Although with the adoption of $\nu_6 = 2343\ \mathrm{cm}^{-1}$ (HCOOH) and $\nu_6 = 2273\ \mathrm{cm}^{-1}$ (DCOOD) we are able to assign more PES band II features than in the initial analysis with $\nu_6 = 1622\ \mathrm{cm}^{-1}$ (HCOOH) and $\nu_6 = 1624\ \mathrm{cm}^{-1}$ (DCOOD), there still remain several features unassigned. These bands, at 3232, 4330 and 5579 cm^{-1} in HCOOH and at 4005 and 5675 cm^{-1} in DCOOD are in high energy regions and probably correspond to combination bands involving some hitherto undetermined mode frequencies. In this respect it is of interest that the interval between the 5579 and 3232 cm^{-1} bands (denoted x' and x, respectively, in Fig. 1b) in HCOOH, $\Delta\nu = 2347\ \mathrm{cm}^{-1}$, corresponds well to $\nu_6 = 2343\ \mathrm{cm}^{-1}$ (Table 4, band II).

4. Conclusion

This study of the He I PES of HCOOH and DCOOD was carried out at a higher energy resolution (15 meV) than previous reported measurements on formic acid. Two spectral regions were explored, Band I corresponding to ionization to the ion ground state $\tilde{\mathrm{X}}\,^2\mathrm{A}'$ of formic acid and Band II where ionization is to the first excited electronic state of the ion, $\tilde{\mathrm{A}}\,^2\mathrm{A}''$. The analysis of observed PES features was carried out on the basis of the spectral implications of structural differences between the calculated geometries of the neutral ground state and of the $\tilde{\mathrm{X}}\,^2\mathrm{A}'$ and $\tilde{\mathrm{A}}\,^2\mathrm{A}''$ states of the formic acid cation [21–23]. The vibronic assignments were helped by parallel analysis of our observed PES of HCOOH and DCOOD, supplemented by data from the less well resolved He I spectra of Watanabe et al. [6] on HCOOD and DCOOH. The vibrational mode frequencies of the $\tilde{\mathrm{X}}\,^2\mathrm{A}'$ and $\tilde{\mathrm{A}}\,^2\mathrm{A}''$ states of HCOOH^+ and DCOOD^+, obtained from the analysis of PES bands I and II are given in Table 6. They obey expected isotopic relations.

The vibrational analysis of band I was straightforward using the approach outlined above. Band II was more difficult to analyse on the simple basis of the carbon–oxygen stretching frequencies expected from correlation with the calculated carbon–oxygen bond lengths, which predicts a decrease of the CO stretch vibrational frequency ν_3 with respect to the neutral ground state. The results are given in assignment A of Tables 4 and 5. However, it proved possible to assign most of the observed band II features for HCOOH and DCOOD after adopting the suggestion of Watanabe et al. [6] that the bands at 2343 cm^{-1} (HCOOH) and 2273 cm^{-1} (DCOOD) be assigned to a carbon–oxygen stretch vibration. This corresponds to an increase in the CO stretch frequency with respect to the neutral species. We speculate that this could occur if the positive charge in the formic acid cation is associated with a carbon–oxygen group.

The analysis of PES band I is consistent with the changes in the structure of formic acid on ionization to the ground state $\tilde{\mathrm{X}}\,^2\mathrm{A}'$ of the cation and provides confidence in the calculations of this ion state carried out by Nguyen et al. [21] and by Takeshita [23]. However, the theoretical calculations of the structure of the first excited state of the ion [22,23], do not lead to satisfactory analysis of the PES band II, as already recognized by

Table 6
HCOOH and DCOOD: vibrational frequencies of the $\tilde{X}\,^1A'$ state of neutral formic acid and the $\tilde{X}\,^2A'$ and $\tilde{A}\,^2A''$ states of the cations

Mode number	HCOOH $\tilde{X}\,^1A'$ (ν/cm^{-1})	HCOOH$^+$ $\tilde{X}\,^2A'$ (ν/cm^{-1})	HCOOH$^+$ $\tilde{A}\,^2A''$ (ν/cm^{-1})	DCOOD $\tilde{X}\,^1A'$ (ν/cm^{-1})	DCOOD$^+$ $\tilde{X}\,^2A'$ (ν/cm^{-1})	DCOOD$^+$ $\tilde{A}\,^2A''$ (ν/cm^{-1})
ν_1	3569			2632 (0.74)[a]		
ν_2	2942	3026		2232 (0.76)	2304 (0.76)	
ν_3	1777	1495[b]	1029	1742 (0.98)	1472 (0.98)	1085 (1.05)
ν_4	1381		1398	945 (0.68)		
ν_5	1223	1196	1296	1040 (0.85)	965 (0.81)	975 (0.75)
ν_6	1104	1495[b]	1622 (A)[c]; 2343 (B)	1171 (1.06)	1472 (0.98)	1624 (1.00); 2273 (0.97)
ν_7	625	510	574	556 (0.89)	447 (0.88)	521 (0.91)
ν_8	1033			873 (0.85)		
ν_9	642			489 (0.76)		

[a] Values in parentheses are the isotopic frequency ratios ν(DCOOD)/ν(HCOOH).

[b] ν_{CO} (see text).

[c] (A) and (B) refer to values given by Assignments A and B of PES band II (cf. Tables 4 and 5 and see text).

Takeshita [23] in his attempt to assign the formic acid PES of Watanabe et al. [6]. In our case, the best analysis of the PES band II (Tables 4 and 5) was assignment B, unexpected on the basis of the theoretical calculations of the structure of the first excited state of the ion. It confirms that the these calculations are of doubtful quality for the structure and dynamics of the excited $\tilde{A}\,^2A''$ state of the cation. This is not altogether surprising in view of the fact that excited electronic state calculations are much more sensitive to configurational interactions than are ground state calculations. An indication of this in the case of formic acid was already evident in the calculations of Peyerimhoff and Buenker [27] mentioned in Section 3.3.2.

Further experimental work is in progress, in particular on the He I PES of the other two isotopomers, HCOOD and DCOOH, and new, more complete theoretical calculations of both the neutral and the cation states of formic acid are in progress. These studies should enable us to refine the analyses presented here, and possibly provide data on other vibrational mode frequencies not determined in the present work.

Finally, we note that our PES observations have provided more accurate values for the first ionization energy of DCOOD and the second ionization energies of HCOOH and DCOOD than previously available in the literature.

Appendix A. Analysis of the threshold photoelectron spectrum of HCOOH and DCOOD in the second ionization energy region

Ruscic et al. [26] measured the TPES of HCOOH and DCOOD in the second ionization energy region between 970 and 1010 Å, with a resolution of 18 meV. Although there is considerable noise in their spectra we were able, from their Figs. 5a (HCOOH) and 6a (DCOOD), to measure the wavelengths of three strong and several weak features in each spectrum. The corresponding energies are given in Table 7. The strong feature at 99 800 (HCOOH) and 99 873 cm^{-1} (DCOOD) are clearly the origin bands of the transitions to the first excited electronic state $\tilde{A}\,^2A''$ of formic acid. Given the shortcomings in measurement from the figures of a publication, these values are in excellent agreement with the origin bands at 99 837 (HCOOH) and 99 852 cm^{-1} (DCOOD) in our PES band II.

Table 7 also includes the frequency intervals $\Delta\nu$ from the origin bands and compares them with those measured in our He I PES. The agreement between these values is very good. The TPES of Ruscic et al. [26] thus confirm the resolved peaks of our PES of HCOOH and DCOOD in the 0–2400 cm^{-1} region.

The TPES exhibits a hot band at −643 cm^{-1} in HCOOH that could be either ν_7, ν_9 or both since

Table 7
Features in the TPES of HCOOH and DCOOD between 970 and 1010 Å [26] and comparison with corresponding features in the He I PES

Band no.	E/eV	E/cm^{-1}	$\Delta\nu$/cm^{-1}	$\Delta\nu$/cm^{-1}
HCOOH TPES band				HCOOH PES band II
1	12.293	99 157	−643	–[a]
2	12.373	99 800	0	0
3	12.448	100 402	602	574
4	12.500	100 817	1017	1029
5	12.545	101 184	1384	1398
6	12.574	101 420	1620	1622
7	12.612	101 729	1929	1898
8	12.664	102 145	2345	2343
DCOOD TPES band				DCOOD PES band II
9	12.331	99 318	−555	–[a]
10	12.383	99 873	0	0
11	12.447	100 392	519	521
12	12.516	100 950	1077	1085
13	12.666	102 163	2290	2273

[a] See text.

$\nu_7 = 625$ cm^{-1} and $\nu_9 = 642$ cm^{-1} in the neutral ground state (Table 1). However, the corresponding hot band in DCOOD at −555 cm^{-1} is unambiguously ν_7, the frequencies of ν_7 and ν_9 being respectively 556 and 489 cm^{-1} in neutral DCOOD (Table 1). There are some hot bands in these frequency difference regions in the He I PES bands I and II, but they are too weak for accurate measurement.

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