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He I photoelectron spectroscopy of four isotopologues of formic acid: HCOOH, HCOOD, DCOOH and DCOOD

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Abstract

He I photoelectron spectra of four isotopologues of formic acid, HCOOH, HCOOD, DCOOH and DCOOD have been measured, mainly with an electron kinetic energy resolution of 15 meV. Quantum chemical calculations of geometries, vibrational mode frequencies and the potential energy distributions characterising each normal mode were made for the neutral $1^1A'$ ground state, the cation ground state $1^2A'$ and first excited ion state $1^2A''$ of the four isotopologues. The results were used to analyse observed vibronic structure in the two PES bands in the 11.3–13.5 eV energy region and this analysis provided values for several vibrational mode frequencies of the ion states. The calculated structure and internal dynamics of the $1^2A'$ ground state of the ion provide satisfactory agreement with experiment but for the $1^2A''$ excited state a more refined theoretical treatment, permitting greater structural flexibility, is required. 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 the four isotopologues. Analysis is also made of PES features concerning the higher energy states of the ions between 12.2 and 21 eV. The adabatic ionization energies of the $2^2A'$, $2^2A''$, $3^2A'$ and $4^2A'$ states in this energy region were determined. Vibrational frequencies were obtained for the $3^2A'$ ion state of the isotopologues and new assignments were made concerning the energy and structure of the $4^2A'$ ion state, whose adiabatic energy was found to lie about 60 meV below the $3^2A'$ state.

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

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previously investigated the He I photoelectron spectra of HCOOH and its isotopologue DCOOD at a higher resolution than that of earlier PES studies [2]. This study has been extended here to two other isotopologues, HCOOD and DCOOH. We were thus enabled to refine and extend the previous assignments of the first two photoelectron bands (Bands I and II, see below) of HCOOH and DCOOD and these are included in a presentation and discussion of the PES of all four isotopologues. In addition, we have analyzed the PES of higher lying ion states for all four isotopologues, providing new information on the energies and photophysics of several of these electronic states. The results of these PES studies are of importance for analysis of the VUV absorption spectra, in particular concerning Rydberg series converging to these ion states [3].

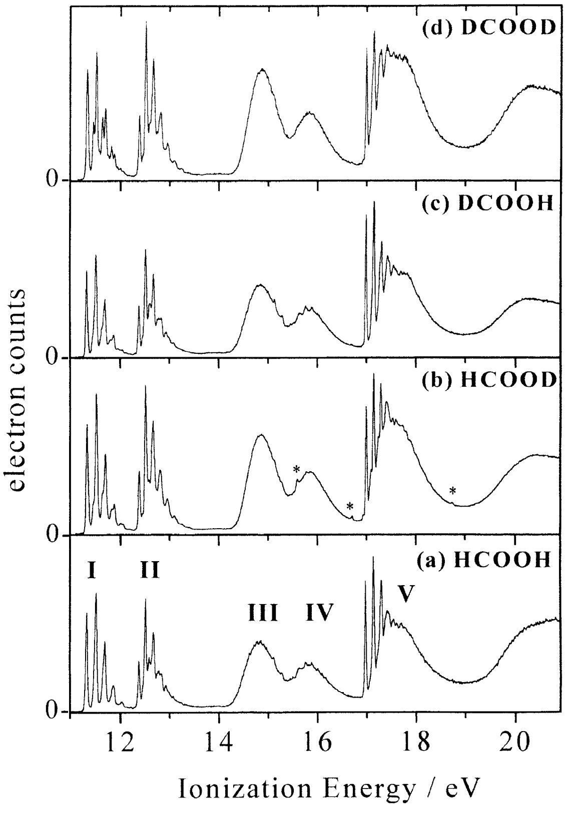

Fig. 1. He I photoelectron spectrum of formic acid: (a) HCOOH; (b) HCOOD; (c) DCOOH; (d) DCOOD. Overview 11–21 eV.

Earlier He I photoelectron spectra of HCOOH have been recorded by Brundle et al. [4] at a resolution of the order of 35 meV, Turner et al. [5] and Thomas [6] (stated resolution ≈40 meV). Watanabe et al. [7] investigated the He I PES of the four isotopologues HCOOH, DCOOD, HCOOD and DCOOH at a stated resolution of 28 meV at the Xe $^2P_{3/2}$ peak at 12.127 eV. Cannington and Ham [8] have measured the relative intensities of corresponding bands in He I (40 meV resolution) and He II (100 meV resolution) photoelectron spectra of formic acid. The energy resolution in our He I PES study of HCOOH, HCOOD, DCOOH and DCOOD is 15 meV. Overview spectra of the the four isotopologues (Fig. 1) were measured at a resolution of 30–36 meV.

2. Experimental

The experimental set-up has been described in detail recently [9]. 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, HCOOD, DCOOH and DCOOD were from Aldrich at the highest available purity. The degree of deuteration of DCOOD is specified to be at least 99%, and 98% that of HCOOD and DCOOH.

The energy calibration of the photoelectron spectra (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 gase IE's 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.

The band energy data in Tables 1–4, respectively for HCOOH, HCOOD, DCOOH and

Table 1
Assignment of photoelectron spectrum Bands I, II and V of HCOOH

Band No.	E/eV	E/cm^{-1}	$\Delta\nu/\mathrm{cm}^{-1}$	Assignment
PES Band I				
1	11.3246	91339	0	$1^2\mathrm{A}'$ 0–0
2	11.3879	91849	510	ν_7
3	11.473	92535	1196	$\nu_5; \nu_6$
4	11.51	92834	1495	ν_3
5	11.6131	93665	2326	$2\nu_5; 2\nu_6$
6	11.6557	94009	2670	$\nu_3 + \nu_5; \nu_3 + \nu_6$
7	11.683	94229	2890	?
8	11.6926	94307	2968	$2\nu_3$
9	11.745	94727	3388	$3\nu_5; 3\nu_6; 2\nu_3 + \nu_7$
10	11.798	95157	3818	$\nu_3 + 2\nu_5; \nu_3 + 2\nu_6$
11	11.838	95479	4140	$2\nu_3 + \nu_5; 2\nu_3 + \nu_6$
12	11.8693	95732	4393	$3\nu_3$
13	11.937	96278	4939	$3\nu_3 + \nu_7$
14	11.9882	96691	5352	$\nu_2 + 2\nu_5$
15	12.0126	96888	5549	$3\nu_3 + \nu_5; 3\nu_3 + \nu_6$
16	12.0452	97151	5812	$4\nu_3$
PES Band II				
17	12.3783	99837	0	$1^2\mathrm{A}''$ 0–0
18	12.4494	100411	574	ν_7
19	12.5059	100866	1029	ν_6
20	12.5516	101235	1398	ν_4
21	12.5794	101459	1622	$\nu_6 + \nu_7$
22	12.6136	101735	1898	$\nu_5 + \nu_7$
23	12.644	101982	2145 inf	$2\nu_6$?
24	12.654	102097	2220 inf	?
25	12.6688	102180	2343	$\nu_3; \nu_4 + \nu_6; \nu_5 + \nu_6$
26	12.7483	102821	2984	$\nu_3 + \nu_7$
27	12.779	103069	3232	ν_2
28	12.8294	103476	3639	$\nu_3 + \nu_4; \nu_3 + \nu_5$
29	12.9151	104167	4330	$\nu_2 + \nu_6$
30	13.07	105416	5579	$\nu_2 + \nu_3$
PES Band V				
31	16.9084	136375	−527	$4^2\mathrm{A}'$ 0–0
32	16.9738	136902	0	$3^2\mathrm{A}'$ 0–0
33	17.05	137517	615	ν_7
34	17.0874	137818	916	ν_5
35	17.1358	138209	1307	ν_6
36	17.2088	138798	1896	$\nu_3; \nu_6 + \nu_7$
37	17.2504	139133	2231	$\nu_5 + \nu_6$
38	17.2929	139476	2574	$2\nu_6$
39	17.3758	140145	3243	$\nu_3 + \nu_6; 2\nu_6 + \nu_7$
40	17.4058	140386	3484	$\nu_5 + 2\nu_6$
41	17.4458	140709	3807	$2\nu_3; 3\nu_6$
42	17.5243	141342	4440	$\nu_3 + 2\nu_6; 3\nu_6 + \nu_7$
43	17.5948	141911	5009	$2\nu_3 + \nu_6; 4\nu_6$
44	17.6828	142621	5719	$3\nu_3$
45	17.7367	143055	6153	?

Inf, inflexion.

Table 2
Assignment of photoelectron spectrum Bands I, II and V of HCOOD

Band No.	E/eV	E/cm^{-1}	$\Delta\nu/\mathrm{cm}^{-1}$	Assignment
PES Band I				
1	11.3307	91388	0	0–0
2	11.3859	91833	445	ν_7
3	11.4451	92310	922	ν_5
4	11.4806	92597	1209	ν_6
5	11.5161	92883	1495	ν_3
6	11.5871	93456	2068	$\nu_5 + \nu_6$
7	11.6305	93806	2418	$\nu_3 + \nu_5; 2\nu_6$
8	11.6621	94061	2673	$\nu_3 + \nu_6$
9	11.6996	94363	2975	$2\nu_3$
10	11.739	94681	3293	$\nu_3 + 2\nu_5; 2\nu_6 + \nu_5$
11	11.7726	94952	3564	$3\nu_6$
12	11.812	95270	3882	$2\nu_3 + \nu_5$
13	11.8397	95493	4105	$2\nu_3 + \nu_6$
14	11.8771	95795	4407	$3\nu_3$
15	11.9916	96718	5330	$3\nu_3 + \nu_5$
16	12.0507	97195	5807	$4\nu_3$
PES Band II				
17	12.3802	99853	0	0–0
18	12.4454	100378	525	ν_7
19	12.5143	100934	1081	ν_6
20	12.5498	101220	1367	ν_4
21	12.5775	101444	1591	$\nu_6 + \nu_7$
22	12.610	101707	1854 sh	$\nu_4 + \nu_7$?
23	12.621	101793	1940 sh	?
24	12.643	101973	2120 sh	$2\nu_6$
25	12.6583	102096	2243	ν_3
26	12.7315	102684	2831	$\nu_3 + \nu_7$
27	12.7866	103130	3277	ν_2
28	12.8142	103353	3500	$\nu_3 + \nu_4$
29	12.881	103892	4039	$\nu_3 + \nu_4 + \nu_7$
30	12.9409	104375	4522[a]	$2\nu_3$
31	13.8085	105501	5648[a]	$\nu_1 + \nu_3$
PES Band V				
32	16.9157	136434	−598	$4\,^2A'$ 0–0
33	16.9899	137032	0	$3\,^2A'$ 0–0
34	17.0542	137551	519	ν_7
35	17.0893	137834	802	ν_5
36	17.142	138259	1227	ν_6
37	17.2044	138762	1730	$\nu_3; \nu_6 + \nu_7$
38	17.2376	139030	1998	$\nu_5 + \nu_6$
39	17.2864	139423	2391	$2\nu_6$
40	17.3449	139895	2863	$\nu_3 + \nu_6; 2\nu_6 + \nu_7$
41	17.3878	140241	3209	$\nu_5 + 2\nu_6$
42	17.4229	140524	3492	$3\nu_6$
43	17.4483	140729	3697	?
44	17.4815	140997	3965	$\nu_3 + 2\nu_6; \nu_3 + 2\nu_6$
45	17.5283	141375	4343	$\nu_5 + 3\nu_6$
46	17.5845	141838	4806	$4\nu_6$?
47	17.620	142112	5080	?
48	17.6473	142334	5302	?

[a] Broad band.

Table 3
Assignment of photoelectron spectrum Bands I, II and V of DCOOH

Band No.	E/eV	E/cm^{-1}	$\Delta\nu/\mathrm{cm}^{-1}$	Assignment
PES Band I				
1	11.327	91358	0	0–0
2	11.389	91858	500	ν_7
3	11.44	92269	911	ν_4
4	11.475	92552	1194	ν_5
5	11.493	92697	1339 inf	ν_6
6	11.503	92781	1423 inf	$\nu_4 + \nu_7$
7	11.514	92866	1508	ν_3
8	11.596	93528	2170	$\nu_4 + \nu_5$
9	11.624	93753	2395	$\nu_3 + \nu_4; 2\nu_5$
10	11.66	94044	2686	$\nu_3 + \nu_6; 2\nu_6$
11	11.695	94326	2968	$2\nu_3$
12	11.781	95020	3662	?
13	11.805	95213	3855	$2\nu_3 + \nu_4$
14	11.84	95496	4138	$\nu_3 + 2\nu_5$
15	11.873	95762	4404	$3\nu_3$
16	12.049	97181	5823	$4\nu_3$
PES Band II				
17	12.379	99843	0	0–0
18	12.45	100415	573	ν_7
19	12.507	100875	1032	$\nu_6; \nu_4$
20	12.58	101464	1621	$\nu_6 + \nu_7$
21	12.607	101682	1839	$\nu_5 + \nu_7$
22	12.665	102150	2307	$\nu_3; \nu_5 + \nu_6$
23	12.738	102738	2895	$\nu_3 + \nu_7$
24	12.773	103021	3178	$\nu_3 + \nu_4$
25	12.82	103400	3557	$\nu_3 + \nu_5$
26	12.914	104158	4315	x (very broad)
27	12.986	104739	4897	$x + \nu_7$
28	13.071	105424	5581	$x + \nu_5$
PES Band V				
29	16.945	136666	−322	4^2A′ 0–0
30	16.9845	136988	0	3^2A′ 0–0
31	17.0603	137599	611	ν_7
32	17.1078	137983	995	ν_5
33	17.1464	138294	1306	ν_6
34	17.222	138904	1916	$\nu_3; \nu_6 + \nu_7$
35	17.2678	139273	2285	$\nu_5 + \nu_6$
36	17.3027	139555	2567	$2\nu_6$
37	17.383	140203	3215	$\nu_3 + \nu_6; 2\nu_6 + \nu_7$
38	17.4149	140460	3472	$\nu_5 + 2\nu_6$
39	17.4554	140787	3799	$3\nu_6$
40	17.5382	141454	4466	$\nu_3 + 2\nu_6; 3\nu_6 + \nu_7$
41	17.574	141743	4755	$\nu_5 + 3\nu_6$
42	17.6853	142641	5653	$\nu_3 + 3\nu_6$
43	17.735	143042	6054	?

Inf, inflexion.

DCOOD, 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

Table 4
Assignment of photoelectron spectrum Bands I, II and V of DCOOD

Band No.	*E*/eV	E/cm^{-1}	$\Delta\nu/\mathrm{cm}^{-1}$	Assignment
PES Band I				
1	11.3353	91425	0	0–0
2	11.3907	91872	447	ν_7
3	11.455	92390	965	ν_5
4	11.49	92675	1250 inf	ν_6
5	11.5178	92897	1472	ν_3
6	11.5744	93353	1928	$2\nu_5$
7	11.6381	93867	2442	$\nu_3 + \nu_5; 2\nu_6$
8	11.7006	94371	2946	$2\nu_3$
9	11.7582	94836	3411	$\nu_3 + 2\nu_5$
10	11.8187	95324	3899	$2\nu_3 + \nu_5$
11	11.86	95657	4232 inf	$\nu_2 + 2\nu_5$
12	11.8771	95795	4370	$3\nu_3$
13	11.9336	96250	4826	$2\nu_3 + \nu_5$
14	11.9931	96730	5305	$3\nu_3 + \nu_5$
15	12.0487	97179	5756	$4\nu_3$
PES Band II				
16	12.3801	99852	0	0–0
17	12.4447	100373	521	ν_7
18	12.5147	100937	1085	$\nu_5; \nu_6$
19	12.5815	101476	1624	$\nu_6 + \nu_7$
20	12.611	101710	1858	$2\nu_5$
21	12.633	101891	2039	$\nu_5 + \nu_6$
22	12.654	102061	2209	$2\nu_6$
23	12.662	102125	2273	ν_3
24	12.7257	102639	2787	$\nu_3 + \nu_7$
25	12.7829	103100	3248	$\nu_3 + \nu_5$
26	12.8082	103305	3453	$\nu_3 + \nu_6$
27	12.8767	103857	4005	?
28	12.9379	104351	4499	$2\nu_3$
29	13.0837	105527	5675	?
30	13.2329	106730	6878	$3\nu_3$
PES Band V				
31	16.924	136501	−533	$4^2\mathrm{A}'$ 0–0
32	16.9901	137034	0	$3^2\mathrm{A}'$ 0–0
33	17.0531	137542	508	ν_7
34	17.0927	137861	827	ν_5
35	17.1094	137996	962	ν_4
36	17.1376	138223	1189	ν_6
37	17.207	138783	1749	$\nu_3; \nu_6 + \nu_7$
38	17.2386	139038	2004	$\nu_5 + \nu_6$
39	17.2541	139163	2129	$\nu_4 + \nu_6$
40	17.2863	139423	2389	$2\nu_6$
41	17.3201	139695	2661	$\nu_3 + \nu_4$
42	17.3561	139986	2952	$\nu_3 + \nu_6; 2\nu_6 + \nu_7$
43	17.3759	140145	3111	$\nu_5 + 2\nu_6$
44	17.4002	140341	3307	$\nu_4 + 2\nu_6$
45	17.4354	140625	3591	$3\nu_6$
46	17.4992	141140	4106	$\nu_3 + 2\nu_6; 3\nu_6 + \nu_7$
47	17.529	141380	4346	$\nu_5 + 3\nu_6$
48	17.5806	141796	4762	$4\nu_6$
49	17.6489	142347	5313	$\nu_3 + 3\nu_6; 4\nu_6 + \nu_7$
50	17.7181	142905	5871	$5\nu_6$
51	17.7548	143201	6167	?

Inf, inflexion.

asymmetric band shapes. We recall that the energy resolution is of the order of 120 cm^{-1}. Thus the accuracy of vibrational intervals derived from measurements of particular shoulders or of broad weak bands is estimated to be no better than ± 20 cm^{-1} and occasionally as much as ± 60 cm^{-1}. Fortunately, the existence of combination and harmonic bands enables more accurate values to be obtained for some vibrational mode frequencies.

3. Theoretical

In the past, there have been a few ab initio quantum mechanical calculations addressing the problem of the electronic and vibrational stucture of formic acid in its neutral and ionized states, in particular in connection with the interpretation of the photoelectron spectroscopy of this species (see Takeshita [10] and references therein). The theoretical picture given by these studies for formic acid and its cation was found to be inadequate for analysis of our experimental findings on these ion states, in particular for the ground and first excited electronic states of the cation, in at least two respects. First, the complete set of mono- and dideuterated isotopologues of formic acid has not previously been studied, in particular for both *cis* and *trans* arrangements of the CH bonds. Second, theoretical artefacts due to the spin-unrestricted approach used to compute zero-order SCF molecular orbitals for the formic acid radical cation can not be eluded, since they can give rise to hazardous spin-contamination effects. These effects can vary appreciably according to the electronic characteristics of the system considered. Excited $HCOOH^+$ radicals of π-type deviate more strongly from the the correct value $\langle S^2 \rangle = 0.75$ than those of σ-type, e.g., ground state formic acid [11,12]. Furthermore, the use of small sets of atomic orbitals worsens the situation.

With the present capabilities of quantum chemistry computer programmes for molecules of medium size, it is now possible to perform ab initio calculations on these species using techniques which attenuate the constraints mentioned above. In the present case, our starting atomic basis is the 6-311++G** set of Gaussian functions, i.e., rather large bases of atomic orbitals which include polarization and diffuse functions in addition to valence shells of the triple-ζ type for both heavy atoms and hydrogen atoms [13]. The occupied and virtual molecular orbitals computed with this set, by means of restricted Hartree–Fock procedures, for the ground state of HCOOH and the ground and first excited states of $HCOOH^+$, provide a preliminary description of their electronic structures, without any spin-contamination effects. For $HCOOH^+$, analogous to the closely related isoelectronic radical systems nitrogen dioxide NO_2 [14], vinoxy CH_2CHO [15] and formyloxyl HCO_2 [16] for which two alternative chemical formulae are predicted at the ROHF level, MC-SCF calculations using the bonding, nonbonding and antibonding π molecular orbitals as active-space components have been carried out. Electron correlation can be taken into account through single and double excitations from the SCF configuration or the set of MC-SCF configurations, using spin-restricted perturbation treatments.

The bond lengths and bond angles of all the structures considered have been fully optimized within the hypothesis of planar geometries of both *cis* and *trans* forms. The corresponding second-derivative matrices (Hessians) give us the theoretical picture, at the harmonic approximation level, of the vibrational properties required for interpretation of our experimental photoelectron spectra results involving the ionic ground and first excited electronic states of the four isotopologues of formic acid. The theoretical vibrational aspects do not include possible spectral shifts due to motions of large amplitude possibly connected to *cis–trans* isomerization, as discussed later.

The quantum mechanical calculations reported in this work have been carried out by means of the routines implemented in the HONDO programme system [17] for generating second-order perturbation values from complete active space procedures [18] equivalent to closed-shell and open-shell SCF treatments. The same programme has been used for the second-order perturbation treatment starting from the set of MC-SCF orbitals. To circumvent the lack of automatic routines for geometry optimizations and Hessian determinations at this level of the theory, we have used the OPTGEN programme which allows such computations by numerical differentiation of the total energy [19].

4. Results and discussion

Our photoelectron spectra of the four isotopologues of formic acid, all given unsmoothed in the respective figures, are shown as an overview in Fig. 1, where the five PES bands are indicated. Detailed spectra of the first (Band I) and second (Band II) PES bands are given in Figs. 2 and 3 respectively, and those of higher energy Bands III, IV and V are presented later. In these figures, the electron counts (spectral intensities) are normalised to the most intense PES band in each spectrum. Visual comparison of published PES of formic acid [4–7] confirm that our resolution is considerably better than in previous studies since bands are resolved in our spectra which are not seen or are only inflexions in published spectra. Comparison with the photoelectron spectra of HCOOH monomers and dimers measured by Thomas [6] 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.

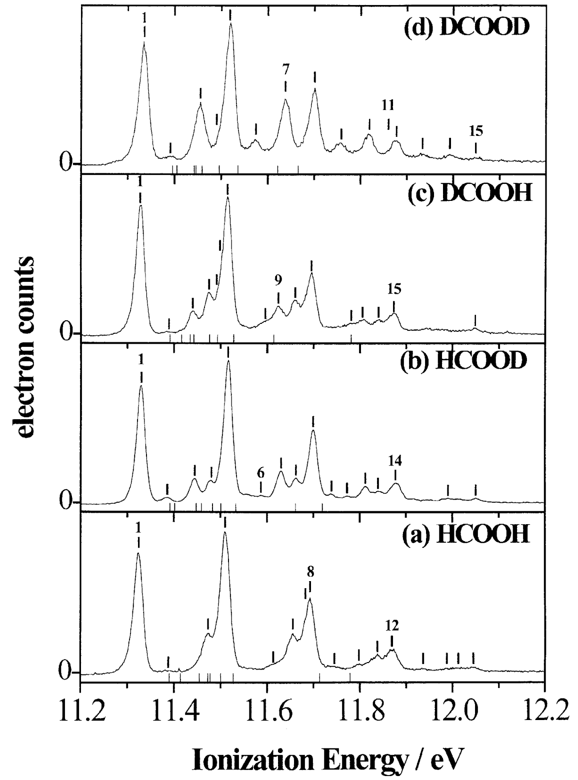

Fig. 2. He I photoelectron spectrum Band I, 11.2–12.2 eV: (a) HCOOH; (b) HCOOD; (c) DCOOH; (d) DCOOD. Vertical bars indicate spectral features listed in Tables 1–4.

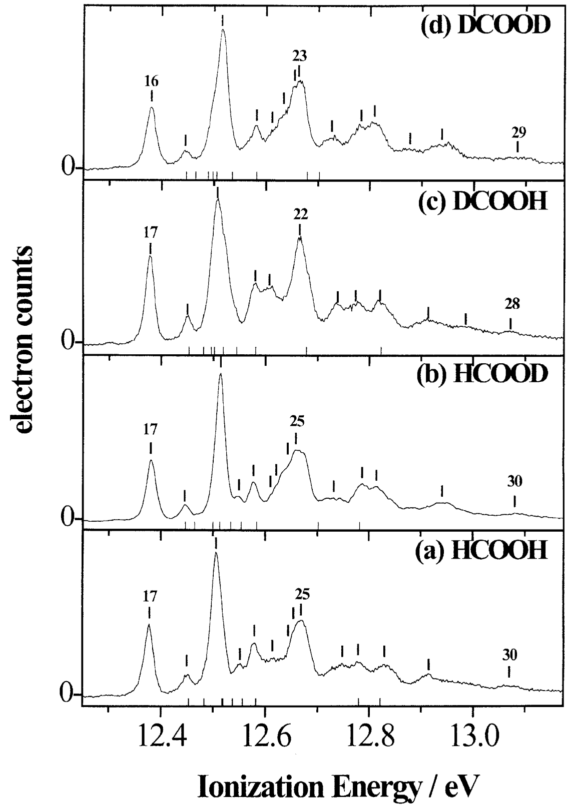

Fig. 3. He I photoelectron spectrum Band II, 12.2–13.2 eV: (a) HCOOH; (b) HCOOD; (c) DCOOH; (d) DCOOD. Vertical bars indicate spectral features listed in Tables 1–4. Band 31 in HCOOD (Table 2) and Band 30 in DCOOD (Table 4) are beyond the energy scale limit of 13.2 eV in the respective (b) and (d).

In the following discussion and analysis of the photoelectron spectra of formic acid, we consider in parallel the observations on the four isotopologues, using the the comparison between the PES features of these isotopologues to strengthen and validate assignments.

4.1. The molecular orbitals of formic acid and their bonding properties

Before entering on a detailed discussion of the photoelectron spectra of formic acid it is necessary to examine its electron configuration, geometrical structure and the experimental and calculated vibrational mode frequencies of the HCOOH ground state $1^1A'$ and of $HCOOH^+$ in its ground $1^2A'$, and first excited electronic state $1^2A''$. This will enable us to predict the structural changes expected on ionization and thus help in assignment of observed photoelectron spectra. We begin with some remarks on the molecular orbitals of formic acid and on the geometrical structure of its ground state.

The ground state of neutral formic acid is planar and belongs to the C_s symmetry group, according to the geometrical stucture determined by microwave spectroscopy of a large set of formic acid isotopologues. Its structure, depicted in Fig. 4 from the work of Davis et al. [20], corresponds to the lowest energy isomer, of *trans* (or *syn*) configuration. The *cis* (or *anti*) isomer of HCOOH lies at 169 meV above the *trans* isomer according to the assignment and relative intensities of weak lines in the microwave spectrum [21,22]. Our calculations, at the MP2 level, give a value of 151 meV for the difference between the *cis* and the *trans* forms.

The electron configuration of HCOOH, in the usually accepted Hartree–Fock approximation canonical orbital energy order [2–4], is as follows:

$$\ldots(6a')^2(7a')^2(8a')^2(1a'')^2(9a')^2(2a'')^2(10a')^2,\ 1^1A'.$$

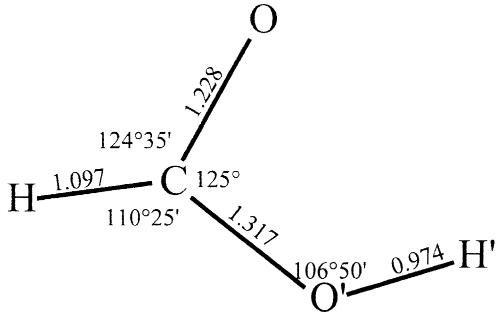

Fig. 4. Experimentally determined structure of the ground state of HCOOH [20]. Internuclear distances in Å units.

According to the ab initio calculations of Demoulin [23], supplemented by those of Itawa and Morokuma [24] and the SCF MO calculations of Kimura et al. [25], 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 localised 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};
- $7a'$ is σ_{C-O};
- $6a'$ is σ_{C-H}.

The two lowest unoccupied molecular orbitals, whose calculated relative energies depend strongly on the basis set used, are:

- $3a''$, which is a π^* MO;
- $11a'$ which is the antibonding in OH analogue of orbital $9a'$.

4.2. Structural changes on ionization to the $1^2A'$ and $1^2A''$ states

We will be concerned with structural changes in the various electronic states of the ion, with respect to the neutral ground state $1^1A'$. We begin with the structural changes expected on ionization to the $1^2A'$ and $1^2A''$ states, for which we have carried out appropriate calculations.

The ground state of the ion has the electron configuration:

$$\ldots(6a')^2(7a')^2(8a')^2(1a'')^2(9a')^2(2a'')^2(10a'),\ 1^2A'$$

and the first excited electronic state is

$$\ldots(6a')^2(7a')^2(8a')^2(1a'')^2(9a')^2(2a'')(10a')^2,\ 1^2A''.$$

The ion ground and first excited states are planar [2].

In Tables 5 and 6 we compare the geometric parameters calculated for the *trans* isomers of the ground and first excited ion states respectively with those of the neutral ground state whose structure is given in Fig. 4. The HCOOH ground state experimental data in column *a* of Table 5 are from the determination of Davis et al. [20] and are

Table 5
Structural parameter values of ground state of neutral HCOOH $1^1A'$ and of ion HCOOH$^+$ $1^2A'$, in *trans* geometry

Parameter	HCOOH $1^1A'^{a}$	HCOOH $1^1A'^{b}$	HCOOH $1^1A'^{c}$	HCOOH $1^1A'^{d}$	HCOOH$^+$ $1^2A'^{b}$	HCOOH$^+$ $1^2A'^{c}$	HCOOH$^+$ $1^2A'^{d}$
r(C=O)/Å	1.204	1.205	1.182	1.179	1.260 (+4.6)	1.260 (+6.6)	1.257 (+4.4)
r(C—O′)/Å	1.342	1.346	1.322	1.321	1.266 (−5.9)	1.245 (−5.82)	1.243 (−5.90)
r(C—H)/Å	1.097	1.101	1.085	1.094	1.099 (−0.2)	1.083 (−0.02)	1.091 (−0.03)
r(O′–H′)/Å	0.972	0.970	0.949	0.952	0.980 (+1.03)	0.960 (+1.16)	0.964 (+1.26)
HCO angle	123.6°	125.1°	124.6°	124.8°	115.4° (−7.75)	116.8° (−6.26)	116.6° (−6.57)
H′O′C angle	106.3°	106.3°	108.9°	108.4°	114.8° (+8.0)	118.5° (+8.82)	117.2° (+8.12)
HCO′ angle	112.0°	109.6°	110.5°	110.3°	118.8° (+8.39)	119.5° (+8.14)	119.5° (+8.34)
OCO′ angle	124.8°	125.3°	124.9°	124.9°	125.8° (+0.4)	123.7° (−0.97)	123.9° (−0.80)

In brackets, percentage changes from calculated neutral values.

[a] Experimental structure [20].

[b] Present work: calculated structures at ROHF/MP2 level. Identical values were obtained at the MCSCF/MP2 level.

[c] Calculated structures [26].

[d] Calculated structures [10].

Table 6
Structural parameter values of ground state neutral HCOOH X^1A' and of ion first excited state HCOOH$^+$ $1^2A''$, in *trans* geometry[a]

Parameter	HCOOH $1^1A'^{b}$	HCOOH $1^1A'^{c}$	HCOOH $1^1A'^{d}$	HCOOH$^+$ $1^2A''^{b}$ ROHF/MP2	HCOOH$^+$ $1^2A''^{b}$ MCSF/MP2	HCOOH$^+$ $1^2A''^{c}$	HCOOH$^+$ $1^2A''^{d}$
r(C=O)/Å	1.205	1.182	1.179	1.334 (+10.7)	1.279 (+6.1)	1.322 (+11.84)	1.327 (+12.55)
r(C—O′)/Å	1.346	1.322	1.321	1.249 (−7.21)	1.299 (−3.49)	1.231 (−5.75)	1.224 (−7.34)
r(C—H)/Å	1.101	1.085	1.094	1.090 (−1.0)	1.089 (−1.1)	1.079 (−0.55)	1.088 (−0.55)
r(O′–H′)/Å	0.970	0.949	0.952	0.989 (+1.96)	0.995 (+2.58)	0.967 (+1.90)	0.969 (+1.79)
HCO angle	125.1°	124.6°	124.8°	122.3° (−2.23)	125.6° (+0.4)	122.0° (−2.09)	121.4° (−2.72)
H′O′C angle	106.3°	108.9°	108.4°	112.7° (+6.02)	110.7° (+4.14)	116.5° (+6.98)	115.7° (+6.73)
HCO′ angle	109.6°	110.5°	110.3°	117.5° (+7.2)	115.6° (+5.47)	118.3° (+7.06)	118.2° (+7.16)
OCO′ angle	125.3°	124.9°	124.9°	120.2° (−4.07)	118.8° (−5.19)	119.7° (−4.16)	120.4° (−3.60)

In brackets, percentage changes from calculated neutral values.

[a] ROHF/MP2 and MCSCF/MP2 level calculated structures of the neutral ground state HCOOH are virtually identical.

[b] Present work: calculated structures.

[c] Calculated structures [27].

[d] Calculated structures [10].

compared with the calculated values determined by us, column b, by Nguyen et al. [26,27], column c, who used the UHF/6-31G** method, and by Takeshita [10], column d, using Roothaan's restricted Hartree–Fock (RHF) method to find the optimum molecular structure. The calculated geometrical parameters of the formic acid ion ground state $1^2A'$ and the first excited $1^2A''$ reported in Tables 5 and 6 are also given in the form of percentage change from the calculated parameter values in the neutral ground state.

Our optimal geometry calculations were carried out for the neutral ground state of HCOOH at the ROHF/MP2 level, and for the ground and first excited states of the ion at.both the ROHF/MP2 and MCSF/MP2 levels. For the ion ground state, the results by the two methods were virtually identical, as expected, since the active space of A' symmetry has been constructed in a similar fashion as for A'' symmetry, i.e., with three π molecular orbitals and one additional σ molecular orbital and, of course, five electrons instead of three. Under these conditions, it is not possible to generate a configuration which mixes appreciably with the basic A' ground-state configurations. The two carbon-oxygen bonds become very similar in bondlength in the ion ground state. Important differences were found in the carbon–oxygen bond lengths calculated for the first excited state of the ion by the two methods. In particular, the C—O bond appears to retain more of its double bond character, with respect to the C—O′ bond in the MSCSF/MP2 calculation, while in the ROHF/MP2 determination, as in those of Nguyen et al [27], the C—O bond, which is a double bond in the neutral ground state, has a much greater length than the C—O′ bond, which is a single bond in neutral formic acid. It appears thus, for both the ground and first excited states of the ion, that the "single" C—O bond should be considered as $\mathrm{C}\overset{\text{—}}{\text{- - -}}(\mathrm{OH})$ and the C═O "double" bond as $\mathrm{C}\overset{\text{—}}{\text{- - -}}\mathrm{O}$ and we will occasionally use this notation.

The HCOOH neutral ground state geometry parameters which we have calculated (Table 5, column b) are very close to the experimental parameters (column a), giving confidence in the calculation techniques. Those calculated by Nguyen et al. [26] and by Takeshita [10] are also reasonably close to the experimental values, but the biggest differences concern the carbon–oxygen bond distances which, as will be seen, are sensitive parameters in our analysis and discussion.

Concerning the formic acid ion ground and first excited states, we see in Tables 5 and 6 relatively little difference between the the percentage changes in the geometrical parameters resulting from our ROHF/MP2 calculations and those derived from the calculations of Nguyen et al. [26] and of Takashita [10]. It follows, from our discussion above, that differences occur in comparing our MCSF/MP2 structural parameters of the excited state of the ion with those of Nguyen et al. [26] and of Takashita [10]. We will return to the question of the structure of the ion excited state in the section interpreting the PES Band II.

4.3. *Vibrational frequencies and their changes on ionization to the $1^2A'$ and $1^2A''$ states*

Column 3 of Table 7 gives the vibrational modes and frequencies of the four isotopologues of neutral formic acid in its ground state, calculated at the ROHF/MP2 level by the methods discussed in Section 3 and, in brackets, the experimental values based on the IR and Raman spectra of several groups [28–31]. Modes 1–7 are in-plane vibrations and have a′ symmetry, while the out-of-plane modes 8 and 9 have a″ symmetry.

Mode assignments of the a′ vibrations both for this state of neutral formic acid and for the ground and first excited states of the isotopologueic cations, were helped by the results of the potential energy distributions (PED) calculated for $\nu_1, \ldots, \nu_7$. The fourth column of Table 7 gives the ROHF/MP2 calculated PEDs for the $1^1A'$ neutral ground state vibrations of the four isotopologues. Experimental and calculated vibrational frequencies are compared in the third column and mode types are given in the second column. The agreement between experimental and calculated values is generally good, the calculated frequencies being mainly less than 5% higher than the experimental values. Takeshita [10] reports calculations of the vibrational frequencies of the totally symmetrical modes of the neutral ground state and the cation $1^2A'$ and $1^2A''$ states of $HCOOH^+$ and $DCOOD^+$. His values are between 5% and 15% greater than ours. The biggest percentage differences are for the two carbon–oxygen stretch vibrations, ν_3 and ν_6, in both electronic states of the ion and for ν_7 in the ion ground state.

The mode types reflect well the principal vibrational contributions to the PED in each case. Takeshita also calculated the PEDs for HCOOH and DCOOD [10] and there is in general good agreement between the two PED results, in particular for the neutral ground state of these two isotopologues.

The PEDs for the $1^2A'$ ground state of the four isotopologueic formic acid ions are presented in Table 8. The vibrational mode numbering corresponds to the mode types of Table 7. It is noticeable that the principal components of the PED of mode 3 include both "single" bond and "double" bond carbon–oxygen vibrational motions, so that it is reasonable to expect, as found both theoretically and experimentally (see later), that mode 3 vibration decreases in going from the neutral to the ion ground state. We also remark that the mode we have classified as mode 4 of HCOOH and HCOOD is far from being a pure δ(HCO) bending vibration since it involves extensive mixing of CO bending and stretching motions in both of these

Table 7
Vibrational modes and frequencies and potential energy distributions (PED) of the $1^1A'$ ground state of neutral formic acid isotopologues: calculated values by ROHF/MP2;[a] frequencies for each isotopologue are listed in order of decreasing value; experimental values[b] are given in parentheses

Mode number	Mode type	HCOOH HCOOD DCOOH DCOOD ν/cm^{-1} [c]	Potential energy distribution
ν_1	ν(OH)	3790 (3569)	0.99 OH
ν_2	ν(CH)	3136 (2948)	0.99 CH
ν_1	ν(OH)	3790 (3570)	0.99 OH
ν_1	ν(OD)	2757 (2632)	0.99 OD
ν_2	ν(CH)	3135 (2942)	0.99 CH
ν_1	ν(OD)	2756 (2632)	0.99 OD
ν_2	ν(CD)	2329 (2220)	0.96 CD
ν_2	ν(CD)	2328 (2232)	0.96 CD
ν_3	ν(C=O)	1809 (1777)	0.89 C=O; −0.25 δ(HCO); 0.23 δ(H′O′C); −0.23 C—O; −0.21 δ(OCO′)
ν_3	ν(C=O)	1803 (1772)	−0.9 C=O; 0.24 δ(HCO); 0.24 C—O
ν_3	ν(C=O)	1781 (1756)	0.87 C=O; −0.23 δ(DCO); −0.26 C—O
ν_3	ν(C=O)	1776 (1742)	−0.89 C=O; 0.23 δ (DCO); 0.27 C—O; −0.20 CD
ν_4	δ(HCO)	1425 (1381)	0.87 δ(HCO); −0.32 δ(H′O′C); 0.33 C=O
ν_4	δ(HCO)	1412 (1360)	−0.95 δ(HCO); −0.28 C=O
ν_5	δ(H′O′C)	1310 (1220)	0.85 δ(H′O′C); −0.34 δ(OCO′); 0.34 C—O
ν_6	ν(C—O)	1199 (1171)	0.77 C—O; −0.41 δ (OCO′); 0.40 δ(DCO); 0.21 C=O
ν_5	δ(H′O′C)	1310 (1223)	−0.7δ(H′O′C); −0.44 C—O; −0.40 δ(HCO); 0.36 δ(OCO′)
ν_6	ν(C—O)	1210 (1178)	−0.8 C—O; 0.51 δ(OCO′); −0.21 δ(D′O′C)
ν_6	ν(C—O)	1180 (1143)	0.68 C—O; 0.48 δ(DCO); −0.35 δ(H′O′C); 0.34 C=O; −0.22 δ(OCO′)
ν_5	δ(D′O′C)	1064 (1040)	−0.63 δ(D′O′C); 0.60 δ(DCO); 0.37 δ(OCO′); 0.30 C=O
ν_6	ν(C—O)	1149 (1104)	0.77 C—O; −0.52 δ(H′O′C); −0.26 δ (OCO′); 0.24 C=O
ν_5	δ(D′O′C)	1009 (990)	0.84 δ(D′O′C); −0.36 C—O; −0.27 C=O; −0.25 δ(OCO′)
ν_4	δ(DCO)	1002 (970)	−0.84 δ(DCO); 0.46 C—O; −0.22 δ(H′O′C)
ν_4	δ(DCO)	972 (945)	0.65 δ(DCO); 0.60 δ(DO′C); −0.45 C—O
ν_7	δ(OCO′)	634 (625)	0.85 δ(OCO′); 0.39 C—O; 0.21 C=O; 0.26 δ(H′O′C)
ν_7	δ(OCO′)	568 (541)	−0.79 δ(OCO′); −0.37 C—O; −0.46 δ(D′O′C)
ν_7	δ(OCO′)	628 (629)	0.86 δ(OCO′); 0.37 C—O; 0.21 C=O; 0.26 δ(H′O′C)
ν_7	δ(OCO′)	564 (556)	0.80 δ(OCO′); 0.45 δ(D′O′C); 0.36 C—O
ν_8	δ(CH)	1063 (1033)	
ν_8	δ(CH)	1060 (1038)	
ν_8	δ(CD)	892 (867)	
ν_8	δ(CD)	892 (873)	
ν_9	δ(OH)	671 (642)	
ν_9	δ(OD)	527 (512)	
ν_9	δ(OH)	662 (625)	
ν_9	δ(OD)	511 (489)	

[a] Vibrational frequencies for modes 8 and 9 calculated at MP2 level. PEDs were not determined for these out-of-plane modes.
[b] From IR and Raman data [28–31].
[c] Listed in groups of four, in the order HCOOH, HCOOD, DCOOH, DCOOD.

ions. Mode 6 contains a considerable component of the carbon–oxygen “double” bond vibrational motion, so that it is reasonable to expect that the mode 6 vibrational frequency increases in going from the neutral to the ion ground state in all four isotopologues.

The data in Table 7 show that the mode frequency dependence of the hydrogen isotope is

Table 8
Vibrational modes and frequencies and potential energy distributions (PED) of the $1^2A'$ ion ground state of formic acid isotopologues: calculated values by ROHF/MP2[a]

Mode number	$HCOOH^+$ $HCOOD^+$ $DCOOH^+$ $DCOOD^+$ ν/cm^{-1}	Potential energy distribution
ν_1	3658	0.99 OH
ν_2	3133	0.99 CH
ν_1	3658	0.99 OH
ν_1	2666	0.99 OD
ν_2	3133	0.99 CH
ν_1	2666	0.99 OD
ν_2	2315	0.98 CD
ν_2	2314	0.98 CD
ν_3	1640	0.68 C—O; −0.58 C=O; 0.44 δ(HCO)
ν_3	1640	0.67 C—O; −0.58 C=O; 0.44 δ(HCO)
ν_3	1625	0.71 C—O; −0.60 C=O; 0.35 δ(DCO)
ν_3	1625	−0.70 C—O; 0.60 C=O; −0.36 δ(DCO)
ν_4[b]	1414	−0.59 C—O; −0.46 δ(H′O′C); 0.45 δ(HCO); 0.40 δ(OCO′); −0.26 C=O
ν_4[b]	1372	−0.66 C—O; 0.52 δ(HCO); 0.42 δ(OCO′); −0.30 C=O
ν_6[c]	1336	0.58 δ(H′O′C); 0.52 C—O; 0.48 C=O; −0.35 δ(OCO′)
ν_6	1291	0.65 C=O; 0.62 C—O; −0.36 δ(OCO′);
ν_6	1223	0.74 C=O; 0.60 δ(HCO); 0.21 C—O
ν_6	1222	0.72 C=O; 0.67 δ(HCO)
ν_5	1199	0.78 δ(H′O′C); −0.53 C=O; −0.33 C—O;
ν_5	996	−0.70 δ(D′O′C); 0.40 C=O; 0.50 δ(DCO);
ν_5	1190	0.8 δ(H′O′C); 0.4 δ(HCO); −0.26 C—O
ν_5	946	0.93 δ(D′O′C); 0.23 δ(HCO); −0.2 δ(OCO′)
ν_4	929	0.89 δ(DCO); 0.34 C=O; 0.22 δ(OCO′)
ν_4	890	−0.75 δ(DCO); −0.63 δ(D′O′C)
ν_7	525	0.90 δ(OCO′); 0.28 C—O
ν_7	489	0.88 δ(OCO′); 0.29 C—O; 0.29 δ(DCO)
ν_7	518	0.89 δ(OCO′); 0.28 C—O; −0.26 δ(DCO)
ν_7	485	0.87 δ(OCO′); 0.29 C—O; −0.21 δ(DCO); 0.29 δ(D′O′C)
ν_8	1046	
ν_8	1035	
ν_8	869	
ν_8	863	
ν_9	721	
ν_9	574	
ν_9	720	
ν_9	562	

Calculated frequencies for each isotopologue are listed in order of decreasing value and in groups of four, in the order $HCOOH^+$, $HCOOD^+$, $DCOOH^+$, $DCOOD^+$.

[a] Mode 8 and 9 vibrational frequencies calculated by UHF method. PED not determined for these out-of-plane modes.

[b] Extensive mixture of CO bending and stretching vibrations; mode classified as ν_4.

[c] Extensive mixture of CO bending and stretching vibrations; mode classified as ν_6.

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. It is useful to note that the vibrational frequencies are similar for the respective modes 1, 5, 6, 7 and 9 for the formic acid isotopologue pair {HCOOH, DCOOH} and, separately, for the pair {DCOOD, HCOOD}, whereas for modes 2, 3, 4, 8 these similarities exist for the isotopologue pairs {HCOOH, HCOOD} and {DCOOD, DCOOH}.

Table 9 gives the calculated PEDs for the first excited state $1^2A''$ of the four isotopologueic ions, where the vibrational mode numbering again corresponds to the mode types of Table 7. The principal components of mode 3 contain both "single" bond and "double" bond carbon–oxygen vibrational motions, but with the C$\overset{\text{——}}{\text{- - -}}$(OH) bond motion now predominating. Thus, one would expect the mode 3 vibrational frequency to decrease even more in the excited $1^2A''$ state than in going from the neutral to the ion ground state $1^2A'$. Whether this expectation is validated experimentally will be discussed later. We note also that the mode we have classified as mode 5 of HCOOH, nominally a $\delta(H'C'O)$ vibration, also involves considerable mixing of other bending and stretching motions in this ion state. In this state, too, mode 6 also contains a considerable component of the carbon–oxygen "double" bond vibrational motion in all four isotopologues.

The ground state $1^2A'$ and the first excited state $1^2A''$ of the cations of the four isotopologues are formed by respective loss of a 10a′ and a 2a″ electron. The sense of our calculated frequency changes, with respect to the neutral ground state, is in good agreement with bonding changes inferred from the bonding properties of the molecular orbitals [2]. We recall that the ion remains planar in both electronic states [2]. Our PED results indicate that the relative intensities of the vibrational components accompanying ionization are likely to differ from isotopologue to isotopologue. A comparison of the calculated ion state vibrational mode frequencies with those extracted from the PES analysis is given later.

Formation of the formic acid ion electronic states $1^2A'$ and $1^2A''$ occur at energies below 12.3 eV. In the 12.3–22 eV region, there are ionization limits corresponding to loss, respectively, of the 9a′, 1a″, 8a′ and 7a′ electrons in one electron transitions. Although there have been calculations of the energies of these ion states, which are, respectively, $2^2A'$, $2^2A''$, $3^2A'$, and $4^2A'$, there are no reported calculations on the structure and vibrational modes and frequencies of these states. In later sections, we will discuss aspects of their structure and vibrational properties as deduced from our photoelectron spectra and from ancillary theoretical and experimental information.

Theoretically calculated structural and vibrational frequency changes between the neutral and ion states help to orient us as to the implications concerning the excitation of particular vibrational modes in the PES Bands I and II concerning respectively the ground and first excited states of the formic acid ion. 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 observations determines the degree of validity of this approach and of the calculations on the formic acid ion states.

4.4. Photoelectron spectra of the four isotopologues: Band I: ion ground state $1^2A'$

The PES Band I corresponds to excitation of the $1^2A'$ ground state of the formic acid ion following loss of a 10a′ electron. Fig. 2, which gives details of Band I of the four isotopologues, also indicates the calculated frequency shifts of the nine vibrational modes of the $1^2A'$ state (Table 8) with respect to the ionization energy (I.E.) peak which is the origin band of this state. The additional information now available from the spectra of the isotopologues HCOOD and DCOOH have enabled us to revise some aspects of our previously published analysis of PES Band I of HCOOH and DCOOD [2].

A key aspect concerns the frequencies of the carbon–oxygen stretch vibrations ν_3 and ν_6 of the $1^2A'$ state. In our earlier publication, we first considered whether, in HCOOH, the strong band at 1495 cm^{-1} and the weaker band at 1196 cm^{-1} from the origin (Fig. 2(a), Bands 4 and 3, respec-

Table 9
Vibrational modes and frequencies and potential energy distributions (PED) of the $1^2A''$ ion first excited state of formic acid isotopologues: calculated values by ROHF/MP2[a]

Mode number	$HCOOH^+$ $HCOOD^+$ $DCOOH^+$ $DCOOD^+$ ν/cm^{-1}	Potential energy distribution
ν_1	3548	0.99 OH
ν_2	3236	0.99 CH
ν_1	3548	0.99 OH
ν_1	2585	0.99 OD
ν_2	3236	0.99 CH
ν_1	2586	0.99 OD
ν_2	2409	0.97 CD
ν_2	2407	0.97 CD
ν_3	1624	0.88 C—O; 0.36 δ(HCO); −0.24 C=O
ν_3	1620	0.86 C—O; 0.38 δ(HCO); −0.25 C=O
ν_3	1608	0.88 C—O; 0.32 δ(DCO); −0.28 C=O
ν_3	1604	0.87 C—O; 0.32 δ(DCO); −0.29 C=O
ν_4	1433	−0.69 δ(HCO); 0.48 δ(H′O′C); −0.39 δ(OCO′); 0.31 C—O
ν_4	1397	−0.82 δ(HCO); 0.37 C—O; −0.36 δ(OCO′)
ν_5	1328	−0.76 δ(H′O′C; 0.40 δ(OCO′); −0.40 C=O
ν_6	1236	0.70 C=O; −0.47 δ(OCO′); 0.36 δ(D′O′C); 0.28 C—O; −0.21 δ(DCO)
ν_5[b]	1273	0.60 δ(HCO); 0.58 δ(H′O′C); 0.50 C=O
ν_6	1225	−0.80 C=O; −0.38 δ(HCO); 0.34 δ(OCO′); −0.30 δ(D′O′C)
ν_6	1116	−0.78 C=O; 0.57 δ(H′O′C);
ν_4	1004	0.74 δ(DCO); 0.55 C=O; −0.32 δ(D′O′C)
ν_6	1122	0.76 C=O; −0.61 δ(H′O′C)
ν_5	952	−0.82 δ(D′O′C); 0.48 C=O; 0.23 δ(OCO′)
ν_4	989	0.92 δ(DCO); 0.27 C=O; −0.22 C—O
ν_5	938	−0.75 δ(D′O′C); −0.54 δ(DCO); 0.28 C=O;
ν_7	589	−0.87 δ(OCO′); −0.30 C—O; −0.29 C=O; −0.23 δ(H′O′C)
ν_7	532	0.82 δ(OCO′); 0.42 δ(D′O′C); 0.30 C—O; 0.22 C=O;
ν_7	584	0.87 δ(OCO′); 0.29 C—O; 0.26 C=O; 0.23 δ(H′O′C)
ν_7	529	−0.80 δ(OCO′); −0.41 δ(D′O′C); −0.30 C—O; −0.20 C=O
ν_8	1116	
ν_8	1074	
ν_8	994	
ν_8	874	
ν_9	845	
ν_9	687	
ν_9	822	
ν_9	684	

Frequencies for each isotopologue are listed in order of decreasing value and in groups of four, in the order $HCOOH^+$, $HCOOD^+$, $DCOOH^+$, $DCOOD^+$.

[a] Mode 8 and 9 vibrational frequencies calculated by UHF method. PED not determined for these out-of-plane modes.

[b] Extensive mixture of δ(HCO) and δ(H′O′C) motions; mode classified as ν_5.

tively) 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 Tables 7 and 8, we expect ν_3 to diminish on ionization and ν_6 to increase. In fact, from a correlation between

CO frequencies and carbon–oxygen bond lengths, we originally considered [2] that the ν_6 frequency could be very similar to, and perhaps even greater than, ν_3 in the ion ground state. However, although the DCOOD PES Band I has a strong band at 1472 cm^{-1} (Fig. 2(d), Band 5), similar in frequency and in intensity to the HCOOH band at 1495 cm^{-1}, there appeared to be no DCOOD feature corresponding to the 1196 cm^{-1} band of HCOOH. From the neutral ground state isotopic frequencies we expected only a small deuterium isotope shift for the carbon–oxygen stretch vibrations. At that time we did not have available good calculations of the vibrational frequencies of the ion states. We were thus led to propose that in the ion ground state the ν_3 and ν_6 frequencies are close in value, so that the 1495 cm^{-1} band in HCOOH and 1472 cm^{-1} band in DCOOD, which have FWHM $\approx$200 and $\approx$180 cm^{-1}, respectively, may each be the superposition of two bands, corresponding to excitation of the ν_3 and ν_6 modes. We noted that the profile of the 1472 cm^{-1} band in DCOOD shows some indication of underlying multiple features. In the published analysis we assigned bands involving these two vibrational modes, which we had inferred as being quasi-degenerate in frequency, with the notation ν_{CO}.

However, the new experimental and calculated data on HCOOD and DCOOH revealed a clear distinction between bands that could naturally be assigned to ν_3 and ν_6 (Figs. 2(b) and (c)). This has led us to assign the key vibrational mode 3, 5 and 6 fundamental vibrational bands in PES Band I of the four isotopologues as follows (calculated frequencies in brackets).

HCOOH. 1196 cm^{-1} is a superposition of ν_5 (1190 cm^{-1}) and ν_6 (1223 cm^{-1}); $\nu_3 = 1495$ (1640) cm^{-1}.

HCOOD. $\nu_5 = 922$ (946) cm^{-1}; $\nu_6 = 1209$ (1222) cm^{-1}; $\nu_3 = 1495$ (1640) cm^{-1}.

DCOOH. $\nu_5 = 1194$ (1199) cm^{-1}; $\nu_3 = 1508$ (1625) cm^{-1}. The ν_6 mode is calculated to be at 1336 cm^{-1}. This is within the profile of the 1508 cm^{-1} band (Fig. 2(c), Band 7), and indeed there is a slight shoulder at about 1339 cm^{-1} (Fig. 2(c), Band 5).

DCOOD. $\nu_5 = 965$ (996) cm^{-1}; $\nu_3 = 1472$ (1625) cm^{-1}. The ν_6 frequency is calculated to be at 1291 cm^{-1}, which is within the profile of the 1472 cm^{-1} band (Fig. 2(d), Band 5) and may correspond to an inflexion at about 1250 cm^{-1} (Fig. 2(d), Band 4).

We stress, in particular, the relative importance of the mode 5 vibration in all four isotopologues, and the difficulty, except for HCOOD, in resolving the mode 6 vibration which falls within the profile of the mode 3 vibration in DCOOH and DCOOD and is superposed on mode 5 in HCOOH. In general, the observed vibrational frequencies are within a few percent of the calculated values, the biggest difference being for the ν_3 mode whose calculated frequencies are 7–10% greater than experimental values. The calculated force field for the ion ground state is thus quite good.

Assignments of PES Bands I for the four isotopologues are given in Tables 1–4. Besides bands giving the fundamental mode frequencies, assignments are also given for harmonics and combination bands. The observed fundamental mode frequencies of the formic acid ion ground state of the four isotopologues are compared with the calculated values in Table 10. There is great consistency between the assignments for the different isotopologues. Discussion of some particular assignments is given below.

4.4.1. The $\delta(H'O'C)$ bending mode vibration ν_5 and the carbon-oxygen stretch vibration ν_6

In our earlier publication, we assigned the 1196 cm^{-1} band of HCOOH (Fig. 2(a), Band 3) exclusively as the H′O′C bending mode vibration ν_5 but our new analysis, based on the spectra of the four isotopologues, assigns this band to both ν_5 and ν_6. Frequencies in this range (±200 cm^{-1}) in the ground state of the $HCOOH^+$ ion are calculated to occur for modes 5 (1190 cm^{-1}), 6 (1223 cm^{-1}) and 8 (1046 cm^{-1}). From the calculated values of mode 8 (Tables 8 and 10), we would expect a band at about 1035 cm^{-1} in HCOOD, 869 cm^{-1} in DCOOH and 863 cm^{-1} in DCOOD. Comparative examination of the spectra indicates that mode 8 is not active or only slightly active and that modes 5 and 6 are active.

The band at 2326 cm^{-1} of HCOOH (Fig. 2(a), Band 5) is assigned as both $2\nu_5$ and $2\nu_6$. The fairly

Table 10
Experimental and, in brackets, calculated[a] vibrational frequencies of the $1^2A'$ ground state of the formic acid cation isotopologues

Mode number	$HCOOH^+$ $1^2A'$ ν/cm^{-1}	$HCOOD^+$ $1^2A'$ ν/cm^{-1}	$DCOOH^+$ $1^2A'$ ν/cm^{-1}	$DCOOD^+$ $1^2A'$ ν/cm^{-1}
ν_1	– (3658)	– (2666)	– (3658)	– (2666)
ν_2	3026 (3133)	– (3133)	– (2315)	2304 (2314)
ν_3	1495 (1640)	1495 (1640)	1508 (1625)	1472 (1625)
ν_4	– (1414)	– (1372)	911 (929)	– (890)
ν_5	1196 (1190)	922 (946)	1194 (1199)	965 (996)
ν_6	1196 (1223)	1209 (1222)	1325 (1336)	1250 (1291)
ν_7	510 (525)	445 (489)	500 (518)	447 (485)
ν_8	– (1046)	– (1035)	– (869)	– (863)
ν_9	– (721)	– (574)	– (720)	– (562)

[a] Calculated for a′ modes 1–7 at ROHF/MP2 level and for a″ modes 8 and 9 at UHF level.

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 in mode 5. The corresponding transitions give rise to separate distinct $2\nu_5$ and $2\nu_6$ bands in the other isotopologues.

We remark that Takeshita [10] predicted three band progressions which he assigned in the only partially resolved HCOOH spectrum of Watanabe et al. [7], and two progressions in the DCOOD spectrum. For HCOOH the 3 progressions were $A = n\nu_3$, $B = \nu_4 + n\nu_3$, $C = \nu_6 + n\nu_3$. The B and C progressions were not resolved in the Watanabe et al. spectrum. The corresponding progressions in our spectrum are assigned, respectively, as $n\nu_3$, in agreement with Takeshita's A progression, $\nu_5 + n\nu_3 (= B)$, and $\nu_6 + n\nu_3 (= C)$, where our "B and C" progressions form quasi-degenerate features. In DCOOD, the two progressions predicted by Takeshita [10] were $A' = n\nu_3$, $B' = \nu_5 + n\nu_3$. We observed these two progressions in our DCOOD spectrum. As is obvious from Figs. 2(a) and (d) and from Tables 1 and 4, our analyses provide assignments for many more features in both HCOOH and DCOOD.

Somewhat similar progressions are found in HCOOD (Fig. 2(b), Table 2) and in DCOOH (Fig. 2(c), Table 3) where, as mentioned above, we observe distinct ν_3 and ν_6 bands as the first members of progressions in $n\nu_3$ and $n\nu_6$ as well as bands corresponding to $\nu_6 + n\nu_3$. The ν_5 mode is active in Band I of both of these isotopologues and ν_4 is clearly active in DCOOH (see later).

4.4.2. The δ (OCO′) bending mode vibration ν_7

We turn now to the assignment of the HCOOH band at around 510 ± 20 cm^{-1} (Fig. 2(a), Band 2) and the corresponding low frequency bands in the other isotopologues: 445 cm^{-1} (HCOOD, Fig. 2(b), Band 2), 500 cm^{-1} (DCOOH, Fig. 2(c), Band 2) and 447 cm^{-1} (DCOOD, Fig. 2(d), Band 2). 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 7). However, a comparison of the observed frequencies and those calculated (Table 8) for modes 7 and 9 of the ion ground state of the four isotopologues argues conclusively in favour of mode 7. The observed ion state frequencies for mode 7 are smaller than those of the neutral ground state for each isotopologue (cf. Table 7), in agreement with the calculated values. The decreased contributions of the carbon–oxygen stretch frequency components in the PED of mode 7 in the ion ground state (Table 8) as compared with the neutral ground state (Table 7) accounts for these ν_7 frequency decreases.

The search for combination bands involving ν_7 revealed the following. Although one can assign quite well $(n\nu_3 + \nu_7)$ $n = 1, 2, 3$ 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} (Fig. 2(d), Bands 6, 9 and 13, respectively), the expected intensity ratios are not observed, due to band overlap. The corresponding isotopic $n = 2, 3$ bands are assigned in HCOOH (Table 1); the $n = 1$ band is probably buried in the high-frequency tail of the strong ν_3 band. No combination bands involving mode 7 could be clearly discerned in the PES Band I of HCOOD and DCOOH. In their expected regions of occurrence there are broad unresolved weak features. The $n\nu_3 + \nu_7$ combination bands therefore appear to be intrinsically weak in the PES I band of the formic acid isotopologues.

The possible assignment of an $\nu_4 + \nu_7$ combination band in DCOOH is discussed below.

4.4.3. The δ (HCO) bending mode vibration ν_4

Mode 4 was not assigned in our previous publication on HCOOH and DCOOD [2]. The new observations on DCOOH, where a distinct band observed at 911 cm^{-1} ((Fig. 2(c), Band 3) could only be assigned to ν_4, its calculated value being 929 cm^{-1}, led us to examine in more detail the possible presence of ν_4 bands in the other three isotopologues. A comparison of observed spectra and calculated frequencies showed that the corresponding mode 4 fundamental band would occur within the profile of strong bands: HCOOH, calculated value 1414 cm^{-1} is within the profile of $\nu_3 = 1495$ cm^{-1} (Fig. 2(a), Band 4); HCOOD, calculated value 1372 cm^{-1} is within the profile of $\nu_3 = 1495$ cm^{-1} (Fig. 2(b), Band 5); DCOOD, calculated value 890 cm^{-1} is within the profile of $\nu_5 = 965$ cm^{-1} (Fig. 2(d), Band 3). Thus, much higher spectral resolution would be necessary in order to discern the ν_4 bands in these three isotopologues of formic acid.

A $\nu_4 + \nu_7$ combination band should appear at 1411 cm^{-1} in DCOOH. This is within the profile of the strong ν_3 band at 1508 cm^{-1} (Fig. 2(c), Band 7). A shoulder at about 1423 cm^{-1} (Band 6) is assigned to this combination band.

4.4.4. Bands involving the OH(OD) and CH(CD) stretch vibrations ν_1 and ν_2

Since the 10a′ molecular orbital is mainly nonbonding n_O on the O atom lone pair of the carbonyl group, and the PED of the ν_2 CH(CD) stretch vibration in the neutral ground state is similar to that of the ion ground state, it is reasonable to predict that the neutral ground state ν_2 frequency will be similar to that in the ion ground state, and that the ν_1 OH(OD) stretch vibration in the neutral and ion ground states might differ more. Certainly, the frequency calculations (Tables 7 and 8) bear out these expectations. Comparison between calculated and experimental values for these two mode frequencies in the neutral ground state lead us to expect that in the ion ground state the ν_1 frequencies will be of the order of 3445, 2645, 3445 and 2545 cm^{-1} for HCOOH$^+$, HCOOD$^+$, DCOOH$^+$ and DCOOD$^+$, respectively. The corresponding expected values for the ν_2 frequencies in the ion ground state will be similar to those observed for the neutral ground state, i.e., 2942, 2948, 2220 and 2232 cm^{-1} for HCOOH$^+$, HCOOD$^+$, DCOOH$^+$ and DCOOD$^+$, respectively.

The fundamental frequency band of ν_1 could be hidden in overlapping strong or weak bands in HCOOH (Fig. 2(a)), HCOOD (Fig. 2(b)) and DCOOH (Fig. 2(c)) but should have been observable in PES Band I in DCOOD, where it is not seen (Fig. 2(d)). We do not see any features that could clearly correspond to the ν_2 fundamental frequencies for the isotopologues but, similar to the case of ν_1, bands close to expected values of ν_2 are observed in each case, including DCOOD. However, their intensities are such that they are best assigned otherwise than to ν_1 and ν_2, as is done in Tables 1–4 respectively. Nevertheless, we assign the 5352 cm^{-1} feature in HCOOH (Fig. 2(a), Band 14) to $\nu_2 + 2\nu_5$ (Table 1), which gives $\nu_2 = 3026$ cm^{-1}. In DCOOD there is a shoulder at 4232 cm^{-1} (Fig. 2(d), (Band 11) which we assign as the corresponding combination band in this isotopologue, giving $\nu_2 = 2304$ cm^{-1} for DCOOD. These frequencies are in satisfactory agreement with our estimated values. The expected corresponding $\nu_2 + 2\nu_5$ bands for HCOOD and DCOOH lie in regions of broad weak features, too indeterminate to provide values of ν_2. 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 and so are not determined in our analysis.

The assignments of vibrational features of the PES Band I provides a number of vibrational frequencies in the 1^2A′ state of the ion for the four isotopologues of formic acid. These frequencies are listed in Table 10 along with the calculated values. Agreement between observed and theoretical vibrational frequencies are good, taking into account the spectral resolution. The calculated frequencies are less than 10% higher than experimental frequencies.

4.5. Band II: ion first excited state $1^2A''$

The first excited ion state, $1^2\mathrm{A}''$, at 12.3783 eV, is formed by loss of a 2a″ electron, and is also planar, according to theoretical calculations [27,28,32].

In Table 6, are given the percentage changes in the structural parameters on ionization to the $1^2\mathrm{A}''$ state, calculated for the *trans* isomer. 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. 4). We might therefore expect to see a more substantial decrease in ν_3(C═O), and a greater increase in ν_6(C—O), with respect to the ion ground state values. This is reflected in the calculated frequencies, where there is an apparent exchange of mode character between modes 3 and 6 in the first excited state of the four isotopologues (Table 9). In addition, the calculated structural modifications in the first excited state suggest that excitation of modes that involve the bond angles could occur, i.e., ν_5, ν_7, ν_8 and ν_9.

The $1^2\mathrm{A}''$ state geometry calculation results of Takeshita [10] are similar to ours (Table 6). However, his simulations of the PES Band II spectrum in the $1^2\mathrm{A}''$ state region of the ion completely fail to reproduce the experimental spectrum of either HCOOH or DCOOD (Fig. 3 of [10]). In the following discussion, we therefore find it not necessary to compare our analyses of the PES Band II with those of Takeshita.

In our previous publication on HCOOH and DCOOD [2] we presented two alternative assignments of PES Band II, denoted as Assignments A and B. Based on the data available at that time we concluded that assignment B was the more probable. The data now available from the PES of HCOOD and DCOOH make possible a more definite assignment of PES Band II, confirming and extending the previous assignment B.

Fig. 3 gives the PES Band II of the four isotopologues, along with indications of the calculated frequency shifts of the nine vibrational modes of the first excited state (Table 9) with respect to the origin band.

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

In the PES Band II of each of the four isotopologues (Fig. 3 and Tables 1–4) the two strongest vibronic bands occur in the 1000–1100 cm^{-1} (≈12.51 eV) and 2300 cm^{-1} (≈12.65 eV) regions, respectively, and a weaker band is found in the 1600 cm^{-1} region (≈12.58 eV). In our previous assignment A of HCOOH and DCOOD PES Band II, we attributed the principal vibrational band in the PES Band II of HCOOH at 1029 cm^{-1} (Fig. 3(a), Band 19) to ν_3, and the weaker Band 21 at 1622 cm^{-1} to ν_6. Similar bands occur in the DCOOD PES Band II at 1085 and 1624 cm^{-1} (Fig. 3(d), Bands 18 and 19, respectively).

However, in that work we found that the strong HCOOH band at 2343 cm^{-1} (Fig. 3(a), Band 25) is difficult to assign unequivocally on the basis of the ν_3 and ν_6 carbon-oxygen stretch vibration assignments of the $1^2\mathrm{A}''$ state given above. This band is broad, with obvious multiple unresolved features (Fig. 3(a)). There is a suspicion of shoulders at 2220 and 2145 cm^{-1} (Fig. 3(a), Bands 24 and 23, respectively). The corresponding band in DCOOD, at 2273 cm^{-1} (Fig. 3(d), Band 23), is also broad, with shoulders at 2209, 2039, 1858 cm^{-1} (Fig. 3(d), Bands 22, 21 and 20, respectively).

This difficulty of assignment was now found to also exist for the corresponding bands of HCOOD and DCOOH. Our analysis of the PES of these species led us to conclude that the best assignments of Band II of HCOOD and DCOOH required adopting the main characteristics of our assignment B made previously in the case of the other two isotopologues. This assignment followed the suggestion of Watanabe et al. [7] that his HCOOH 2369 (our 2343) cm^{-1} band be assigned to a CO vibration. Bands of similar intensity in this frequency region were also reported by Watanabe et al. [7] for the four isotopologues.

The interpretation of our PES Band II for the four isotopologues of formic acid is made with the

≈2300 cm^{-1} band being assigned to ν_3 (Tables 1–4). In our earlier work, we listed this frequency as ν_6 on the basis that the structural changes on ionization to the $1^2A''$ state could make $\nu_6 > \nu_3$, and in an attempt to provide mode parentage relations. The actual mode numbering of the CO stretch vibrations in the ion states is somewhat arbitrary, however, as discussed earlier (cf. the PEDs in Tables 7–9) and we now list the ≈2300 cm^{-1} frequency as ν_3, with the 1100–1250 cm^{-1} frequency as ν_6, the calculated nominal ν_6 values (Table 9) being closer to this frequency range.

The large discrepancy between the calculated ν_3 values (1600–1650 cm^{-1}) and the experimental values ≈2300 cm^{-1} require an explanation. The apparent unusual first excited state internal dynamics involving carbon-oxygen stretch vibrations led us to consider structural reasons for this behaviour. 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} [33], so that it is not impossible for a 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 [34] stress that the 2a″ molecular orbital will be strongly mixed with the 3a″ (π_3^*) MO, 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. Our calculations of charge distributions in the $1^2A''$ state indicate that loss of the 2a″ electron gives rise to the appearance of about 0.22 positive charge on the carbon, 0.45 charge on the carbonyl oxygen and 0.33 charge on the other oxygen atom. This confirms that there is a charge transfer from oxygen to carbon in the first excited electronic state of the ion.

Another consideration is based on a remark of Takeshita [10], which he made on the basis of the calculations of Nguyen [26,27] on 1,3-hydrogen shifts in the ground and first excited state of the $HCOOH^+$ ion. Takeshita concluded that for mode 3, the harmonic oscillator approximation is reasonable for the ground state but not for the excited state of the ion. He suggested that in the latter there is a double minimum in the potential energy curve for mode 3 vibration. In following up this suggestion, we considered whether the *cis* form of the ion excited state was close in energy to that of the *trans* form so that a low barrier between them could lead to double minima behaviour and/or large vibrational anharmonicities. We calculated the structural parameters of the *cis* form of the $1^2A''$ state, at the ROHF/MP2 level, and found the bond lengths and bond angles to be very similar to those of *trans*, taking into account the new orientation of the H′O′C angle in the *cis* form. The calculated energies showed that the *cis* form of the $1^2A''$ state lies 1371 cm^{-1} above the *trans* form. At this level of calculation of the $1^2A''$ state, the resulting bond angles are not reliable and there is no evidence for double minima and/or large vibrational anharmonicities in the excited state potential energy surface. The basic problems in valid calculations of the excited state concern obtaining adequate structural flexibility so as to be able to deal with large amplitude vibrations. The effective Hamiltonian must take all rovibronic couplings into account, which requires using a 2-dimensional Hamiltonian. This would provide a single potential energy surface for the $1^2A''$ state rather than one for each of two separate structures. It represents a programme for future work. For the moment our analysis of PES, Band II must remain on an empirical basis, justified by experiment. We will assume that the major discrepancies between experiment and theory are limited to the modes 3 and 6 vibrations, so that we will use the calculated frequencies for the other vibrational modes in Table 9 to assist us in the analysis of the PES Band II of the four isotopologues.

4.5.2. Bending vibrational modes

The low frequency bands at 574 cm^{-1} (HCOOH, Fig. 3(a), Band 18), 525 cm^{-1} (HCOOD, Fig. 3(b), Band 18), 573 cm^{-1} (DCOOH, Fig. 3(c), Band 18) and 521 cm^{-1} (DCOOD, Fig. 3(d), Band 17) agree well with the respective calculated ν_7 frequencies, 589, 532, 584 and 529 cm^{-1} (Table 9). The ratio $R = \nu_7(\text{observed})/\nu_7(\text{calculated}) = 0.975,\quad 0.987,$ 0.981 and 0.985, respectively for the isotopologues and their consistency confirms the assignment to ν_7.

There is greater activity of this mode than in the ion ground state. Watanabe et al. [7] report very weak bands in HCOOH (544, 631 cm^{-1}), HCOOD (544, 530 cm^{-1}), DCOOH (649, 772 cm^{-1}) and DCOOD (518, 534 cm^{-1}) which they consider as possibly being due to O—C—O bending vibrations. We only observe one band in this spectral region for each of the four isotopologues and indeed, in the published spectra of Watanabe et al. a second feature is not obvious. We note that only one feature is observed in this region in the threshold photoelectron spectra of HCOOH, at 602 cm^{-1}, and DCOOD, at 519 cm^{-1} [35], as discussed in our earlier paper [2]. In any case, the second feature frequencies listed by Watanabe et al. are very much lower than those expected from our calculations (Table 9) for ν_9, the mode of next higher frequency.

The weak but clear band at 1398 cm^{-1} in HCOOH (Fig. 3(a), Band 20) is assigned to the δ(HCO) bending vibrational mode ν_4. This assignment leads us to expect the corresponding band in DCOOD to occur at about 1000 cm^{-1}, according to the calculated frequencies given in Table 9. This feature would lie, unresolved, in the low-frequency part of the strong 1085 cm^{-1} band profile (Fig. 3(d), Band 18). A similar situation occurs for DCOOH, where the ν_4 band, expected at about 990 cm^{-1}, would be within the profile of the strong 1032 cm^{-1} band (Fig. 3(c), Band 19). In HCOOD, a ν_4 band, calculated to be at about 1390 cm^{-1}, is clearly seen at 1367 cm^{-1} (Fig. 3(b), Band 20)

4.5.3. Combination bands

On adopting the ν_3 and ν_6 values of assignment B, we were able to assign many combination bands, e.g., the band in the 1600 cm^{-1} region in the four isotopologues can be assigned as $\nu_6 + \nu_7$, while bands at 2984 (HCOOH), 2831 (HCOOD), 2896 (DCOOH) and 2787 (DCOOD) cm^{-1} could be assigned to $\nu_3 + \nu_7$. These and other combination bands, some of which involve ν_4, ν_5 and/or ν_2 are given in Tables 1–4.

There still remain several features unassigned, in particular a broad band in DCOOH peaking at 4315 cm^{-1} (Fig. 3, Band 26) and the very broad DCOOD bands at 4005 cm^{-1} and 5675 cm^{-1} (Fig. 3(b), Bands 27 and 29 respectively). These are in high energy regions and possibly correspond to combination bands involving some hitherto undetermined mode frequencies.

The vibrational frequencies of the $1^2A''$ state of the ion for the four isotopologues of formic acid, determined from analysis of PES Band II, are given in Table 11 along with the calculated values. Taking into account the spectral resolution, agreement between observed and theoretical vibrational frequencies are reasonable, except for the carbon-oxygen stretching modes 3 and 6, the reasons for which are discussed in Section 4.5.1. In this connection, it is interesting to note that for

Table 11
Formic acid isotopologues: experimental vibrational frequencies of the $1^2A''$ state of the cations from analysis of PES Band II and, in brackets, calculated values[a]

Mode number	$HCOOH^+$ $1^2A''$ ν/cm^{-1}	$HCOOD^+$ $1^2A''$ ν/cm^{-1}	$DCOOH^+$ $1^2A''$ ν/cm^{-1}	$DCOOD^+$ $1^2A''$ ν/cm^{-1}
ν_1	– (3548)	– (2546)	– (3548)	– (2585)
ν_2	3232 (3236)	3277 (3236)	– (2409)	– (2407)
ν_3	2343 (1624)	2243 (1620)	2307 (1608)	2273 (1604)
ν_4	1398 (1433)	1367 (1397)	1032 (989)	– (1004)
ν_5	1324 (1273)	– (952)	1266 (1328)	929 (938)
ν_6	1029 (1122)	1081 (1225)	1032 (1116)	1105 (1236)
ν_7	574 (589)	525 (532)	573 (584)	521 (529)
ν_8	– (1116)	– (1074)	– (994)	– (874)
ν_9	– (874)	– (687)	– (822)	– (684)

[a] Calculated for a′ modes 1–7 at ROHF/MP2 level and for a″ modes 8 and 9 at UHF level.

each of the isotopologues the experimental frequencies of mode 6 are notably smaller than their calculated counterparts, while the experimental frequencies of mode 3 are considerably greater than their calculated values. The calculated frequencies of some other modes are quite close to some frequencies observed for other, more active, modes so that the corresponding bands could be hidden in the profile of the stronger bands. Taking this possibility into account, one could suggest the following: in HCOOD the 1081 cm^{-1} band (Fig. 3(b), Band 19) also contains ν_5, while for DCOOH the strong 2307 cm^{-1} band (Fig. 3(c), Band 22) also contains ν_2, and in DCOOD ν_2 is hidden in the strong band at 2273 cm^{-1} (Fig. 3(d), Band 23).

4.6. Higher energy PES bands of the four isotopologues of formic acid

Our PES above the second ionization energy are shown as Bands III, IV and V in the overview spectra given in Fig. 1.

We recall that photoelectron spectroscopy has established a series of ion states arising by successive loss of an electron from molecular orbitals of HCOOH : $\ldots(6a')^2(7a')^2(8a')^2(1a'')^2(9a')^2(2a'')^2(10a')^2$. In the previous sections we have dealt with the PES corresponding to loss of an electron from the 10a′ and 2a″ molecular orbitals, below 12.3 eV. In the 12.3–22 eV region, the ionization corresponding to loss of one of the 9a′, 1a″, 8a′ and 7a′ electrons gives rise to formation of the $2^2A'$, $2^2A''$, $3^2A'$ and $4^2A'$ states, respectively. The PES relevant to these states is analyzed and discussed for the four isotopologues of formic acid in the next sections.

Considering briefly even higher ionization energies, we note that loss of the 6a′ electron would occur close to or above 22 eV since it is calculated to take place at a (vertical) energy about 4.5 eV above that of the 7a′ electron loss [34,36], which is in the 17 eV region (see below). Therefore loss of a 6a′ electron can be estimated to occur at about 21.5 eV, which is outside our observational range in this He I PES study. In this study we neglect any satellite states corresponding to two-electron transitions and configurational effects in general, which is reasonable for HCOOH below 22 eV [37]. States which are associated with loss of the inner valence electrons 5a′ and 4a′ give rise to many satellite bands whose intensities are distributed over the 30–40 eV region in high energy PES [37,38]. Inner shell electrons of HCOOH, in orbitals 1a′, 2a′ and 3a′ have ionization energies that are calculated to be of the order of 300 eV (3a′) or greater (2a′, 1a′) [34,36].

4.7. PES band III: Ion third excited state $2^2A'$

The He I PES shows a broad band in the 14.2–15.3 eV region (Band III), peaking at 14.81 eV in HCOOH and at similar energies for the other three isotopologues (Fig. 5): 14.84 eV in DCOOH; 14.86 eV in HCOOD; 14.84 eV in DCOOD). This band corresponds to loss of a 9a′ electron and formation

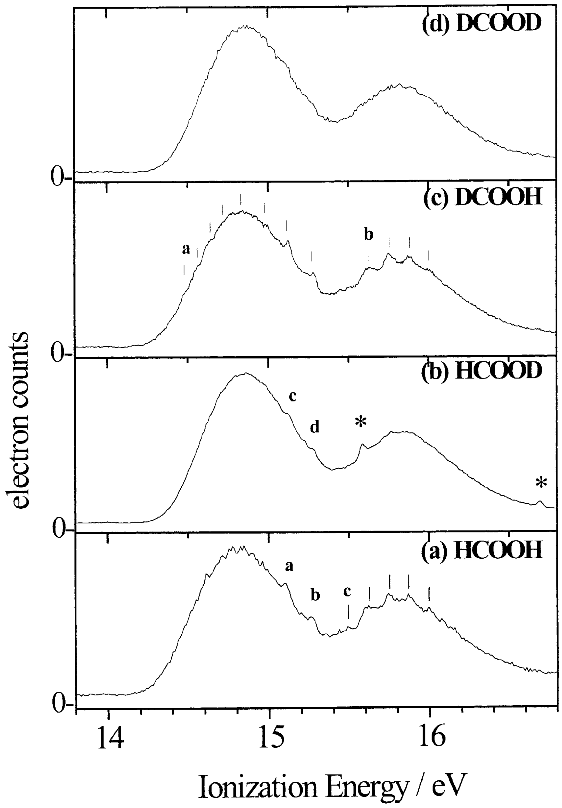

Fig. 5. He I photoelectron spectrum Bands III and IV, 14.0–16.8 eV, from Fig. 1, enlarged: (a) HCOOH; (b) HCOOD; (c) DCOOH; (d) DCOOD.

of the 2^2A′ ion state. In the He I PES of HCOOH and of HCOOD in the 14.2–15.3 eV region, we find little evidence of vibrational structure of the 2^2A′ ion state except for two peaks, at 15.102 and 15.258 eV in HCOOH (features *a* and *b* in Fig. 5(a)) which are also clearly seen in Brundle et al. [4], and at 15.119 and 15.277 eV in HCOOD (features *c* and *d* in Fig. 5(b)), whose intervals are of the order of 1260 and 1274 cm^{-1} respectively. There is more structure in the 14.2–15.3 eV region in DCOOH (Fig. 5(c)) where we observe shoulders or small peaks, whose positions are indicated by vertical bars, (the first, marked *a,* is at 14.478 eV), that have successive intervals 659, 662, 631, 911, 1194, 1073, 1274 cm^{-1}. This last interval is similar in position and value to the 1260 and 1274 cm^{-1} intervals in HCOOH and HCOOD. The DCOOD spectrum in the 14.2–15.3 eV region shows no obvious vibrational features (Fig. 5(d)). The observed vibrational component in the 1200–1300 cm^{-1} range in the other isotopologues is most probably the ν_6 carbon–oxygen stretch vibration. The 600–660 cm^{-1} intervals in DCOOH, which are of ill-defined shoulders, may possibly involve the the ν_7 vibration.

We note that Brundle et al. [4] give 940 cm^{-1}, and Turner et al. [5] 950 cm^{-1}, as the principal vibrational frequency for both this and the 2^2A″ ion state of HCOOH$^+$, although it is clear that their spectra contain the same two Band III peaks a and b (see above) are seen as in our HCOOH PES where our measured interval is 1260 cm^{-1}. We remark that the principal vibrational intervals in the 2^2A″ ion state of HCOOH are in the 960–1080 cm^{-1} range (see below).

4.8. PES Band IV: ion state 2^2A″

From the He I PES Band IV of formic acid HCOOH (Fig. 5(a)), we measure the vertical IE to be 15.75 eV for forming the 2^2A″ state, and estimate the adiabatic IE to be at about 15.35 eV. Similar values are found for the other three isotopologues (Figs. 5(b–d) and Table 12). Vibrational features are more evident than for the 2^2A′ state. In HCOOH, the 2^2A″ state PES exhibits 5 vibrational bands (Fig. 5(a)), whose measured successive intervals are 1080, 1016, 960 and 1016 cm^{-1}, the initial band, marked *c* in Fig. 5(a), being at 15.63 eV. These intervals are of the order of magnitude of the 940 cm^{-1} [4] and the tentative 950 cm^{-1} [5] values reported, repectively, by Brundle et al. [4] and by Turner et al. [5] for Band IV, as noted above. In DCOOH (Fig. 5(c)), we observe four vibrational bands in the peak region, whose successive frequency intervals are 1016, 1032 and 936 cm^{-1}, which are very similar to the corresponding vibrational intervals in HCOOH,

Table 12
Adiabatic ionization energies of the formic acid isotopologues

Ion state	HCOOH *E*/eV	HCOOD *E*/eV	DCOOH *E*/eV	DCOOD *E*/eV
1^2A′	11.3246 *11.33*[a] (11.35)[b] [11.33][c]	11.3307	11.3272	11.3353
1^2A″	12.3783 *12.37*	12.3802	12.3793	12.3801
2^2A′	≈14.15 *≈14.2*	≈14.2	≈14.2	≈14.2
2^2A″	≈15.35 *≈15.4*	≈15.4	≈15.4	≈15.4
3^2A′	16.9738 *16.97*	16.9907	16.9864	16.9901
4^2A′	16.9084	≈16.921	≈16.911	16.924

[a] In italics, data from Brundle et al. [4].

[b] in curved brackets, data from Thomas [6].

[c] in square brackets, data from Watanabe et al. [43].

while for HCOOD (Fig. 5(b)) there are two peaks due to N_2 impurities (at 15.5866 and 16.6961 eV) but no obvious HCOOD vibrational features in this region. The PES in the corresponding region of DCOOD (Fig. 5(d)) was too noisy for detection of vibrational veatures.

Assignment of the observed vibrational features cannot be made with certitude, but the fact that the observed intervals are similar in HCOOH and DCOOH make it probable that the excited mode is ν_5 or ν_6. Other modes should be more sensitive to deuterium substitution of the hydrogen atom attached to the carbon atom as is the case for the neutral and ion ground states (Tables 7 and 8) and the ion excited $1^2A''$ state (Table 9).

4.9. PES Band V: ion fourth excited state $3^2A'$

Loss of a 8a′ electron gives rise to the $3^2A'$ state. The He I PES Band V shows well defined vibrational bands in the region 16.9–18.0 eV region for all four isotopologues (Fig. 6), with a notable background that peaks at about 17.6 eV (see later). In HCOOH, the adiabatic I.E. of the $3^2A'$ state is 16.971 eV (Table 12). Isotopic shifts of this adiabatic I.E. are discussed in Section 4.11.

Measurement of the HCOOH PES Band V shows a progression of strong bands with successive intervals 1307, 1267, 1233, 1202 cm^{-1} (Fig. 6(a), Bands 35, 38, 41, 43), evidently a carbon–oxygen stretch vibration, which we consider to be ν_6. In addition, there is observed a similar progression which appears to be a combination with a vibrational frequency 916, 924, 910 cm^{-1} (Fig. 6(a), Bands 34, 37, 40) that is most probably ν_5 (see later). Thus there are progressions in $n\nu_6$ and in $\nu_5 + n\nu_6$ (Table 1). There are also weaker bands at 615, 589, 669, 633, 710 cm^{-1} intervals (possibly ν_7, see later) associated with the respective principal bands of the $n\nu_6$ progression. Another important feature is an apparent "hot band" at −527 cm^{-1} (Fig. 6(a), Band 31) with respect to the state origin band.This "hot band" is also seen in the HCOOH PES Band V of Turner et al. [5].

Similar features are observed in Band V of the other formic acid isotopologues. In HCOOD, the $n\nu_6$ progression frequency intervals are 1227, 1164, 1101 cm^{-1} (Fig. 6(b), Bands 36, 39, 42). Combination bands are observed displaced by 802, 771, 818 cm^{-1} (Fig. 6(b), Bands 35, 38, 41) from the respective terms of the $n\nu_6$ progression and are considered to form the $\nu_5 + n\nu_6$ progression. A "hot band " is observed at −598 cm^{-1}. (Band 32). In DCOOH the $n\nu_6$ progression vibrational band intervals are 1306, 1261, 1232 cm^{-1} (Fig. 6(c), Bands 33, 36, 39). There are $\nu_5 + n\nu_6$ combination bands at intervals 995, 979, 905 cm^{-1}, respectively, from the main $n\nu_6$ progression bands, and other combination bands at 611 and 610 cm^{-1} with respect to the main progression. A distinct "hot band" peak is not observed for DCOOH but there is a "hot band" shoulder at about −322 cm^{-1} (Fig. 6(c), Band 29) in the origin band profile with respect to its peak frequency (Band 30).

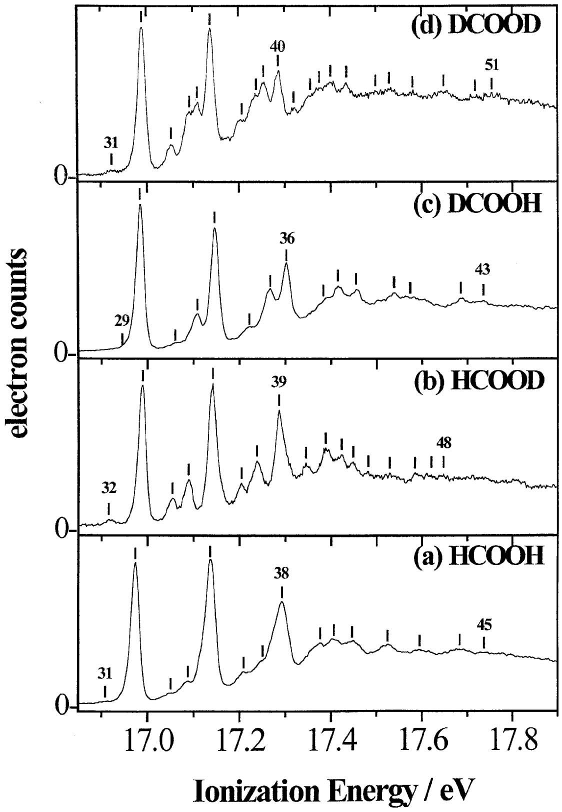

Fig. 6. He I photoelectron spectrum Band V, 16.8–17.9 eV: (a) HCOOH; (b) HCOOD; (c) DCOOH; (d) DCOOD. Vertical bars indicate spectral features listed in Tables 1–4.

In DCOOD, the $n\nu_6$ progression vibrational band intervals are 1189, 1200, 1202, 1171, 1109

cm^{-1} (Fig. 6(d), Bands 36, 40, 45, 48, 50) and $\nu_5 + n\nu_6$ combination bands at 962, 940, 918 cm^{-1}, respectively from the main $n\nu_6$ progression bands (Table 4). There are other combination bands at intervals of 827, 815, 722, 755 cm^{-1} (Bands 34, 38, 43, 47) and at 508, 560, 563 cm^{-1} with respect to the main progression. A "hot band" is observed at -533 cm^{-1} (Band 31).

The frequencies found in the combination with the $n\nu_6$ main progression bands were assigned to the specific vibrational modes given above according to their isotopic behaviour and their order of magnitude. On this basis the vibrational frequency of 1307 cm^{-1} in HCOOH, 1227 cm^{-1} in HCOOD, 1306 cm^{-1} in DCOOH, and 1189 cm^{-1} in DCOOD corresponds to the carbon-oxygen stretch ν_6 vibrational mode in the $3^2A'$ ion state, while the following group of frequencies, $\approx$920 cm^{-1} in HCOOH, 802 cm^{-1} in HCOOD, 995 cm^{-1} in DCOOH, $\approx$770 cm^{-1} in DCOOD, fit best an assignment to ν_5. The HCOOH frequency 650 ± 50 cm^{-1}, 519 cm^{-1} in HCOOD, 611 cm^{-1} in DCOOH and the DCOOD frequency 535 ± 30 cm^{-1} are probably ν_7 frequencies. Their isotopic behaviour mirrors that of the neutral ground state ν_7 frequencies.

The vibrational frequencies observed for the $3^2A'$ ion state are gathered together in Table 13. Most of these frequencies are similar to those of the corresponding vibrational modes in the neutral ground state of the various isotopologues, being less than 10% different from the latter. The exception is ν_5, which is about 20% smaller than in the neutral isotopologues. This behaviour of ν_5, which is essentially a $\delta(H'O'C)$ deformation vibration, is readily understandable from the σ_{OH} bonding character of the 8a′ electron ejected in forming the $3^2A'$ ion state.

The apparent hot bands at -527 cm^{-1} in HCOOH, -598 cm^{-1} in HCOOD, ≈ -322 cm^{-1} in DCOOH and -533 cm^{-1} in DCOOD do not fit the neutral ground state frequencies and their isotopic behaviour given in Table 7. We consider them to be origin bands of the $4^2A'$ ion state (see below).

The existence of well-resolved vibrational structure in the $3^2A'$ ion state part of PES Band V of the four isotopologues of formic acid implies that this ion state has a relatively long lifetime. This has bearing on the interpretation of the photoelectron–photoion coincidence (PEPICO) study by Nishimura et al. [39] of the breakdown curves of HCOOH up to 19 eV, in bringing up some interesting photophysical aspects, and is discussed elsewhere [40].

4.10. PES Band V: ion fifth excited state $4^2A'$

The precise energy of the $4^2A'$ state resulting from loss of a 7a′ electron is not clear from the experimental viewpoint. Experimental values in the literature are stated to be for vertical ionization of HCOOH and are quoted as: $\approx$17.7 eV [4], 17.8 eV [6], 17.49 eV [41]. A distinct $4^2A'$ state is not evident in the PES of these authors but in these previous studies it is assumed to occur in the energy region where there is a modification in the regularity of the PES Band V vibrational bands initially belonging to the $3^2A'$ state [4,6,25].

Table 13
Formic acid isotopologues (PES Band V at 17 eV): experimental vibrational frequencies of the $3^2A'$ state of the cations

Mode number	$HCOOH^+$ $3^2A'$ ν/cm^{-1}	$HCOOD^+$ $3^2A'$ ν/cm^{-1}	$DCOOH^+$ $3^2A'$ ν/cm^{-1}	$DCOOD^+$ $3^2A'$ ν/cm^{-1}
ν_1				
ν_2				
ν_3	1896	1730	1916	1749
ν_4				962
ν_5	916	802	995	827
ν_6	1307	1227	1306	1189
ν_7	615	519	611	508
ν_8				
ν_9				

There are several calculated values for the energy difference between the $4^2A'$ state and the $3^2A'$ states: 0.68 eV [4]; 0.98, 1.213 eV [34]; 0.734 eV [36]; 0.67, 0.81, 1.06 eV [25]. These are evidently vertical ionization differences. Experimental values of $\Delta E(v) = E(4^2A'–3^2A')$, the energy difference between the apparent vertical I.E.s of these two states in the He I PES of HCOOH are quoted in the literature as 0.2 eV [41]; 0.57 eV [4]; 0.6 eV [6].

We have stated above that the apparent hot bands in Fig. 6 at -527 cm^{-1} in HCOOH, -598 cm^{-1} in HCOOD, ≈ -322 cm^{-1} in DCOOH and -533 cm^{-1} in DCOOD relative to the origin band of the $3^2A'$ ion state could be the origin bands of the $4^2A'$ ion state. In this case, since these "hot bands" lie at energies below the origin band of the previously denoted $3^2A'$ ion state we should nominally invert the numbering of these states but, for convenience, we will retain the previous designation of the $3^2A'$ ion state.

From the "hot bands", we derive the following values of the $4^2A'$ ion state origin band energies, which we consider as adiabatic I.E.s as given in Table 12: HCOOH: 16.9084 eV; HCOOD: 16.9157 eV; DCOOH: 16.944 eV; DCOOD: 16.924 eV. From the values given in Table 12, we derive the following values for ΔE(ad) the $3^2A'–4^2A'$ state adiabatic energy difference: HCOOH: 65 meV; HCOOD: 74 meV; DCOOH: 40 meV; DCOOD: 66 meV. These are small energy differences. However, the vertical energy differences are much larger, as discussed below.

Our assignment of the $4^2A'$ ion state in the four isotopologues is consistent with the following observations and arguments.

The $3^2A'$ state PES features exhibit a strong origin band. The ionization is due to loss of a 8a′ electron, whose MO is essentially σ_{OH}, which would not much affect the O—C—O structure, and its potential hypersurface, with respect to the neutral ground state. However, the $4^2A'$ state corresponds to loss of a 7a′ electron, whose M.O is essentially $\sigma_{C–O}$. This would affect the OCO skeleton so that the $4^2A'$ ion state potential surface would be displaced with respect to the neutral ground state OCO structure. From the Franck–Condon principle we can therefore predict that the PES transition to the $4^2A'$ state would give rise to an extended photoelectron spectral envelope, as is indeed observed. It is noticeable that the loss of the 9a′ electron, whose MO is also σ_{CO}, forming the $2^2A'$ ion state also gives rise to a broad photoelectron spectral band, in the 14.2–15.3 eV region (Band III), with not very marked vibrational structure, as was discussed in Section 4.7.

We thus consider that the background in PES Band V in the 17–18 eV region, which rises to a maximum at about 17.6 eV in each of the four isotopologues (Fig. 6), contains the PES of the $4^2A'$ ion state. Some of the weak vibrational features in Band V may be vibrational features of the $4^2A'$ state, superimposed on this broad PES background. We remark that in Band V there are vibrational features all the way up to about 17.8 eV in HCOOH, 18 eV in HCOOD, 17.82 eV in DCOOH, 18 eV in DCOOD, whereas in the previous section, we have assigned vibrational features in the $3^2A'$ state only up to to about 17.6 eV for each of the isotopologues (Tables 1–4).

The energy of the maximum at about 17.6 eV in the PES background can be considered as the vertical energy of the $4^2A'$ ion state. We can therefore discuss the measured vertical energy differences with respect to the origin band of the $3^2A'$ state PES, ΔE(v). The experimental $3^2A'–4^2A'$ vertical energy differences are as follows: HCOOH: ≈626 meV; HCOOD: ≈500 meV; DCOOH: ≈600 meV; DCOOD: ≈ 660 meV. We can compare them with several calculated values for the vertical energy difference between the $4^2A'$ state and the $3^2A'$ state of $HCOOH^+$: 0.68 eV [4]; 0.98 eV, 1.123 eV [34]; 0.734 eV [36]; 0.67 eV, 0.81 eV, 1.06 eV [25]. The observed vertical differences for the four isotopologues are close to the 680 meV calculated value of Brundle et al. (Koopmans' theorem vertical ionization potential reduced by 8% [4]) and the 670 meV value of Kimura et al. calculated by an SCF MO [6-31 G] method [25]. The calculation results provide support for our interpretation of the PES in the 17 eV region.

4.11. Adiabatic ionization energies of formic acid isotopologues

The adiabatic ionization energies of the four isotopologues of formic acid from our PES are reported in Table 12, which also contains the few existing literature values of the adiabatic energies. Accurate adiabatic transition energies were obtained for those states that have clearly observed origin bands, i.e., the $1^2A'$ ground state and the $2^2A''$, $3^2A'$ and $4^2A'$ excited states, as discussed in detail above.

The isotopic shifts for the $1^2A'$ ground state and the $1^2A''$ first excited state of the ion are compatible, within experimental error, with the differences between the estimated zero-point energies of the neutral ground state and these ion states. These zero-point energies, estimated as one-half the sum of the calculated vibrational frequencies for each state and isotopologue (Tables 8 and 9), provide zero-point energy differences between 193 and 227 cm^{-1} for the ion ground state minus neutral, and 59 to 81 cm^{-1} for the first excited state of the ion minus neutral. Experimental and, in brackets, calculated differences between the observed ion state energies of HCOOH and the corresponding states of the other isotopologues (HCOOD, DCOOH, DCOOD) are between −49 (−17), −21 (−17), −86 (−34) cm^{-1} for the ground state of the ion, and −15 (−11), −8 (+11), −15 (+3) cm^{-1} for the first excited state. We recall that although the energy resolution in our PES study is 15 meV (120 cm^{-1}), the measurement precision of the sharp peak positions is 2 meV (16 cm^{-1}).

The value of the first ionization energy (I.E.) of formic acid (HCOOH), determined from Rydberg band analysis of absorption spectra, is reported as 11.329 ± 0.002 eV [42]. The first excited state of the ion has a reported appearance energy of 12.37 eV [4]. Our observed PES values for these two ionization energies are 11.3246 and 12.3783 eV, respectively (Table 12), 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, and the second ionization energy of HCOOH are the most accurate yet reported, as are the values for HCOOD and DCOOH, which are the first reported for these two isotopologues. We remark that no I.E. values were reported by Watanabe et al. [7] for the three deuterated isotopologues.

The adiabatic energies of the $2^2A'$ and $2^2A''$ states are not accurately known, so that isotopic shifts cannot be determined for these states. The adiabatic energy which we report for the vibrationally well-structured $3^2A'$ state of HCOOH (Table 12) is in good agreement with that given by Brundle et al. [4]. As discussed above, we have determined for the first time a value for the adiabatic energy of the $4^2A'$ state (Table 12).

The values of the differences between the adiabatic energies, with respect to HCOOH, of the $3^2A'$ state are −136 cm^{-1} (HCOOD), −102 cm^{-1} (DCOOH) and −131 cm^{-1} (DCOOD). For the $4^2A'$ state they are −102 cm^{-1} (HCOOD), −21 cm^{-1} (DCOOH) and −126 cm^{-1} (DCOOD), which are similar to the respective values for the $3^2A'$ state, except for DCOOH which has the least well observed $4^2A'$ state origin band. These isotopic differences have the same sign and are somewhat greater than those given above for the $1^2A'$ and $1^2A''$ states. We cannot compare observed with calculated values since, as mentioned earlier, there are no calculations of the vibrational frequencies of the $3^2A'$ and $4^2A'$ states of formic acid.

5. Conclusion

This study of the He I photoelectron spectra of four isotopologues of formic acid was carried out at a higher energy resolution than previous reported measurements on formic acid. Two spectral regions where considerable vibrational structure is observed in the PES were explored at a resolution of 15 meV: between 11.2 and 13.2 eV, containing Band I which corresponds to ionization to the ion ground state $1^2A'$ of formic acid and Band II where ionization is to the first excited electronic state of the ion, $1^2A''$, and between 16.8 and 18.2 eV, where Band V characterises the $3^2A'$ and $4^2A'$ states of the ion. Bands III and IV, in the 14 to 16.5 eV region, involve ionization to the $2^2A'$ and $2^2A''$ states, respectively, and were measured at a resolution of 30–36 meV. The analysis of observed PES vibrational features in Bands I and II 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 $1^2A'$ and $1^2A''$ states of the formic acid cation and of calculated vibrational mode frequencies and the corresponding potential energy distributions of these states of the four isotopologues HCOOH, HCOOD, DCOOH and DCOOD. The vibronic assignments in Bands I, II and V were helped by parallel analysis of our observed photoelectron spectra of the four isotopologues.

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 the calculations. 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. [7] that the strong bands in the 2300 cm^{-1} region observed at $\approx$12.67 eV in Band II of all four isotopologues 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 $1^2A''$ state is associated with the carbon-oxygen groups, as appears to be the case from our calculation results. It is suggested that for the calculations to provide reasonable values for the carbon-oxygen stretch frequencies in the $1^2A''$ state, Hamiltonians must be used that take into account multidimensional rovibronic couplings. These would make it possible to derive potential energy surfaces appropriate for dealing with large amplitude vibrational motions and eventually possessing double minima.

The most interesting part of the higher energy region concerned Band V, which was shown to involve both the $3^2A'$ and $4^2A'$ ion states. The extensive vibrational structure associated with the $3^2A'$ state was analysed and provided vibrational mode frequencies which are similar to those of the corresponding modes in the neutral ground state, except for mode 5 whose behaviour reflects the σ_{OH} bonding character of the 8a′ electron which is lost on formation of this electronic state of the ion. We determined, for the first time, the adiabatic energy of the $4^2A'$ state and showed that it lies about 60 meV below the $3^2A'$ state. We note, further, that our PES observations have provided more accurate values for the first ionization energy of DCOOD and the second and higher ionization energies of HCOOH and DCOOD than previously available in the literature. The corresponding data which we measured for the ionic states of the HCOOD and DCOOH isotopologues, has never previously been reported.

Finally, we mention that our PES results and analysis have proved to be important in the analysis of the absorption spectrum [3] and VUV photophysics [40] of formic acid.

Acknowledgements

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