Vibrational Structures in the He(I) Photoelectron Spectra of Carboxylic Acids

Iwao Watanabe, Yu Yokoyama, and Shigero Ikeda
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560

(Received August 17, 1973)

The first and the second bands of the photoelectron spectra of acetic, propionic, and isobutyric acids were recorded, and the vibrational structures in the spectra were studied by comparing with the results of formic acid. The first band exhibits a $\nu_{C=O}$, a δ_{OH}, and a ρ_{COOH} vibrational progression, and this implies that an oxygen lone pair orbital, from which the first band of the spectra originates, contributes not only to a C=O bonding and the bonding between carbonyl oxygen and hydroxyl hydrogen, but to the settling of carboxyl group in the molecular plane. The second band exhibits a $\nu_{C=O}$, a ν_{C-O}, and a δ_{OCO} vibrational progression with very high frequency for the $\nu_{C=O}$ as observed in the case of formic acid. Thus the vibrational features of the second band are consistent with the ionization of an antisymmetric π orbital localized mainly on carbonyl and hydroxyl oxygen atoms. Since the 0-0 vibrational transitions for the second ionization are out of the Franck-Condon region, the second adiabatic ionization potential was estimated by comparing the vibrational fine structures of the spectra with that of formic acid. The second adiabatic ionization potential of acetic acid so determined is 11.63 eV.

It is predicted from theoretical calculations that the most easily ionized orbitals, from which the first and the second bands of photoelectron spectra of aliphatic carboxylic acids originate, are an oxygen lone pair (n_O) and an antisymmetric π (π_2) orbital.[1–3] It is reasonable to expect that these bands have quite similar appearances among these molecules, since the calculations predict that the n_O orbital is localized mainly on a carbonyl oxygen and the π_2 on carbonyl and hydroxyl oxygens. In other words, if some features in the photoelectron bands are found which are common in all carboxylic acids, they must be the features intrinsic to the carboxyl group.

In the previous report,[3] the vibrational structures in the spectra of formic acid and its deuterium derivatives have been studied in detail, and the most interesting phenomenon found in the spectra of formic acid is the extraordinarily strengthened C=O bond by the ionization of the π_2 orbital. If the n_O and the π_2 orbitals are really the intrinsic orbitals localized on the carboxyl group, similar vibrational structures to those of formic acid should be revealed in the spectra of acetic acid and/or higher carboxylic acids, too.

The only vibrational structures reported in the spectrum of acetic acid are a $\nu_{C=O}$ (C=O stretching vibration) mode in the first band, and a 1050 cm^{-1} mode unassigned in the second.[4,5] Any other vibrational structures in the second or deeper bands for acetic or higher carboxylic acids have not been reported.

This paper deals with the first and the second bands of improved resolution spectra of acetic, propionic, and isobutyric acids together with the comparison of their fine structures with those of formic acid to find intrinsic features in the photoelectron spectra of carboxylic acids.

Experimental

The photoelectron spectra were measured with an apparatus already reported[6] and a modified helium resonance lamp. The new lamp has a shorter collimating capillary of wider inner diameter and two hollow electrodes aligned in the optical axis of the lamp. The modification increased the intensity of the exciting light (He(I) 584 Å), and better performance was attained.

All samples were of G. R. grade and used without any further purification. Variations of appearance potentials of photoelectron peaks for carboxylic acids during measurements were so large that preliminary mixing of reference gas, xenon, into the sample gas was essentially needed to measure the ionization potentials accurately. Usually the spectra were measured after running of sample gas more than 30 minutes, since shift of the kinetic energy of photoelectron to lower energy side with the elapse of time was always noticed. The measurements were repeated many times for more than five hours until it was confirmed that the differences between consecutive runs were not detected.

The point which an attention should be paid to is the dependence of the resolving power of this apparatus on the sample pressure. The spectra of acetic acid at high and low pressures have very different appearances. The spectrum at low sample pressure has adequate signal intensity and very similar appearance to the expanded spectrum reported by Sweigart *et al.*[4] On the other hand, the high pressure spectrum has sharper bands with finer vibrational structures. To study whether the association of sample molecules or the change of sample density in an ionization chamber gives rise to the phenomenon, the sample gas was mixed with xenon gas and the spectra of the sample were measured with varying the xenon gas pressure while the partial pressure of the sample gas remained constant. It was found that by introducing the xenon in relatively high pressure the spectrum features resemble those of the high pressure spectrum, and that the resolving power strongly depends on the gas density in the ionization chamber. The similar phenomena have been noticed in the cases of other molecules. The factors influencing the variation of the electron kinetic energy[6] can cause the broadening of the photoelectron peaks. It was found that the degree of the photoelectron spectrum degradation by the broadening depends on the character of the sample gas, the gas density in the ionization chamber, and the history of the apparatus, that is, the sample flowed just before the measurement, the period of the apparatus left at rest in vacuum or in air, and so on.

Results and Discussion

The First Bands. The expanded spectra of the first band of acetic, propionic, and isobutyric acids are shown in Figs. 1, 2, and 3, respectively, and their vibrational frequencies are summarized in Table 1. The spectra of other aliphatic carboxylic acids do not exhibit clear vibrational structures and are not shown.

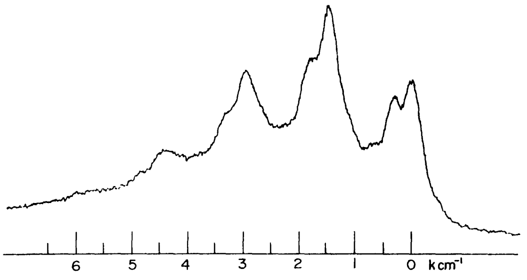

Fig. 1. The first band of the photoelectron spectrum of acetic acid.

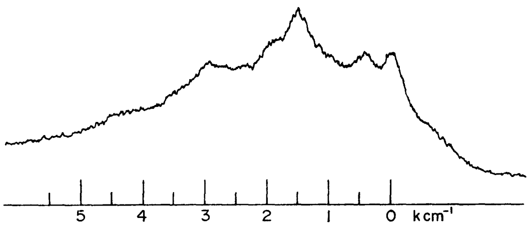

Fig. 2. The first band of the photoelectron spectrum of propionic acid.

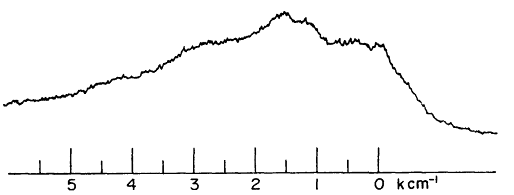

Fig. 3. The first band of the photoelectron spectrum of isobutyric acid.

For comparison the fundamental vibrational frequencies of the ground molecular state of acetic acid are taken from the work by Berney *et al.*,[7] which utilized an inert-gas matrix method and are included in Table 1. The usual gas phase IR spectra of the monomers of carboxylic acids have been measured at a high temperature, 150 °C, to decrease dimer equilibrium ratio and thus the appearance of their IR spectra becomes broad and complex. The matrix-isolation technique at temperatures near 4 K sharpens the absorption peaks, removes hot bands, and allows an accurate determination of the band origins.

Obviously the first ionization is accompanied by the excitation of not only a $\nu_{C=O}$ mode but some other vibrational modes in all carboxylic acids. The main spacings (*ca.* 1500 cm^{-1}) of the $\nu_{C=O}$ present in all molecules almost agree with that of formic acid (1486 cm^{-1}).[3]

The frequencies for the next strongest vibrational progression are 310, 420, and 360 cm^{-1} in acetic, propionic, and isobutyric acid, respectively. This structure has not been reported yet. It is difficult to find a fundamental mode of acetic acid corresponding to such a low vibrational frequency and thus the two possibilities are considered to interpret this low frequency component by attributing to one of the vibrational frequencies of dimer molecule. (1) The photoelectron spectra of dimers of carboxylic acids have the same profiles as those of monomers with the ionization potential blue shifted by *ca.* 38 meV (~300 cm^{-1}). The orbital energies, obtained from the *ab initio* MO calculations performed by Ady *et al.*,[8] of the highest occupied σ orbital of monomer and dimer molecule of formic acid are −0.4510 and −0.4526 (in atomic units) and the difference is about the same as the observed ionization potential shift. (2) The adiabatic ionization potentials of monomers and dimers are almost or just the same and thus the peaks separated

Table 1. Vibrational frequencies in the first band spectra of some carboxylic acids, and fundamental frequencies of ground state acetic acid[a] (cm^{-1})

Acetic	Propionic	Isobutyric	Assignments
1500±20	1500±30	1510±40	$\nu_{C=O}$
1470±20	1430±40		
1450±30			
310±20	420±30	360±40	ρ_{gear}
320±40	430±50		
380±50			
1170±50	1090±100	1150±50	δ_{OH}
1190±50	1170±50		
710±50	850±50		ν_{CC}, ν_{C-O}, or ρ_{CH3}
730±50			
910±50			

a′ block						a″ block		
ν_1	ν_{OH}	3583	ν_7	ν_{C-O}	1259	ν_{13}	ν_{HCH2}	2996
ν_2	ν_{HCH2}	3051	ν_8	δ_{OH}	1181	ν_{14}	δ_{HCH2}	1439
ν_3	ν_{CH3}	2944	ν_9	ρ_{CH3}	987	ν_{15}	ω_{CH3}	1044
ν_4	$\nu_{C=O}$	1788	ν_{10}	ν_{CC}	847	ν_{16}	τ_{OH}	535
ν_5	δ_{HCH2}	1434	ν_{11}	δ_{OCO}	581	ν_{17}	γ	639
ν_6	δ_{CH3}	1380	ν_{12}	ρ_{gear}	428	ν_{18}	τ_{CH3}	93

a) From C. V. Berney, R. L. Redington, and K. C. Lin, Ref. 7.

from the main progression by 300—400 cm^{-1} correspond to the vibrational components of dimer ions.

Although low frequency modes are easily found in the IR or Raman spectra of dimers,[9-11] both explanations mentioned above are based on the assumption of very near or almost equal ionization potentials for monomer and dimer molecules and this is unlikely if the photoelectron experiment of carboxylic acid dimers performed by Thomas[5] is considered. His spectra for dimers are very broad and structureless and he has concluded that the ionization potentials of dimers are 0.2—0.3 eV lower than those of the corresponding monomers. The peaks observed in the present spectra should have been broadened if the peaks were attributed to the dimers, because of many low frequency hydrogen bond vibrations of dimer ions and the thermal population of the low frequency vibrational states of the dimer molecules.

Therefore above-mentioned two models are discarded and the low frequency mode is more likely to be attributed to the monomer ions. The present experiments in which the pressure of ionization chamber was changed by introducing inert gas strongly support that the spectra obtained are from monomers.

This low frequency structure is not observed in the spectrum of formic acid, and then should originate from the vibration accompanying the geometrical alteration of methyl group. With regard to a ν_{17} (γCOOH wagging) or a ν_{18} (τ_{CH_3}, CH$_3$ torsion) among the modes in an a$''$ block their doubled frequencies are too high or too low[12] compared with 310 cm^{-1} and it is unlikely that the vibrational mode of a$''$ symmetry is so strongly excited by the ionization of the n$_0$ orbital.

It is concluded, therefore, that the most reasonable assignment is a ν_{12} (ρ gear, COOH rocking or CCO angle deformation). Other modes in an a$'$ block are thought to arise from vibrations involving more rigid bonds and are too high frequencies. This ν_{12} mode excitation in acetic acid could be considered to be an evidence supporting the assignments that the first band of formic acid exhibits not only a δ_{OH} but a δ_{CH} vibrational component.[3]

Another structure observed in all spectra of the three carboxylic acids is *ca.* 1100 cm^{-1} vibration and this mode could be assigned as a δ_{OH} by analogy with the case of formic acid.[3] The peaks appear weakly as shoulders on the slopes of the $\nu_{C=O}$ progression in formic and acetic acid, and are separated from the peaks of the $\nu_{C=O}$ progression by the deuterium substitution of hydroxyl hydrogen in the formic acid molecule.

The remaining vibration unassigned, 700—900 cm^{-1}, could be attributed either to a ν_{CC}, a ρ_{CH_3} (CH$_3$ rocking), or a ν_{C-O}.

A broad band in Figs. 2 or 3 at the lower ionization potential region than a 0-0 peak might be attributed to the ionization of corresponding dimer, since the appearance is quite similar to that of the mixture of monomer and dimer molecules reported by Thomas.[5]

The Second Bands. The appearances of the second band spectra of acetic, propionic, and isobutyric acids are quite different from that of formic acid, but the three spectra resemble each other. At least six vibrational peaks are clearly distinguishable in the spectrum of acetic acid. The vibrational analysis assuming the first or the second peak as arising from an adiabatic ionization process have not led to any reasonable vibrational assignments.

Then, for the identification of the position of the 0-0 peak, namely, the adiabatic ionization potential, the second band spectrum of acetic acid has been superimposed on that of formic acid and the best fit obtained is shown in Fig. 4, together with the bands of propionic and isobutyric acids. It is shown in Fig. 4 that the vibrational fine structures in the spectra of the three acids are quite the same as that of formic acid, and that the 0-0 transition for acetic and higher carboxylic acids is out of the Franck-Condon region.

The adiabatic ionization potential of the second band of acetic acid so determined is 11.63 eV and is included in Table 2 with other ionization potentials determined by the same procedures.

The vibrational assignments are summarized in Table 3. The frequencies measured in practice are the peak separations from the postulated 0-0 peak and therefore the small differences of the frequencies of formic acid

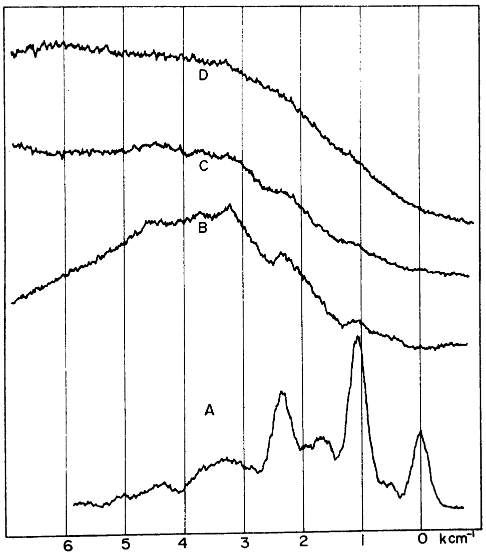

Fig. 4. The second bands of the photoelectron spectra of A; formic acid, B; acetic acid, C; propionic acid, and D; isobutyric acid.

TABLE 2. IONIZATION POTENTIALS FOR n$_0$ AND π_2 ORBITALS OF SOME CARBOXYLIC ACIDS (eV)

		Acetic	Propionic	Isobutyric
n_0	Adiabatic	10.664±0.003	10.525±0.003	10.329±0.005
	Vertical	10.848±0.003	10.711±0.003	10.519±0.005
π_2	Adiabatic	11.63 ±0.01	11.52	11.39
	Vertical	12.02 ±0.01	11.91	12.80

TABLE 3. VIBRATIONAL FREQUENCIES IN THE SECOND BAND OF ACETIC ACID SPECTRUM (cm^{-1})

Frequencies from 0—0 peak (postulated)	Assignments
510	δ_{OCO}
1050	ν_{C-O}
2320	$\nu_{C=O}$
3260	$\nu_{C-O}+\nu_{C=O}$ (3370)
3760	$\nu_{C-O}+\nu_{C=O}+\delta_{OCO}$ (3770)
4500	$2\nu_{C=O}$ (4640)

from those of acetic or other carboxylic acids do not have any significance.

The spectra in Fig. 4 become broad and structureless as the substituted alkyl group becomes larger, but still the band structures seem to correspond well to those of formic acid.

Thus the vibrational modes appearing in the second band for the molecules from formic to isobutyric acid are a $\nu_{C=O}$, a ν_{C-O}, and a δ_{OCO}, and are all fundamental modes intrinsic to the main framework of carboxyl group.

Conclusion

The technique of photoelectron spectroscopy provides the information about the structures of various ions produced by the ionization of one of the electrons in the corresponding molecule. This capability of the technique could be described in other way that the technique is able to give the information how each electron plays a role in the molecule.

From the study of the photoelectron spectra it is concluded that the n_0 and the π_2 orbitals have a number of inherent properties common to all the carboxylic acids studied.

1. The photoelectron spectra of carboxylic acids have a characteristic band, n_0, of carboxyl group corresponding to the first ionization and the n_0 orbital is so separated in energy from other deeper orbitals that the corresponding photoelectron band always appears as a strong isolated band overlapped by no other bands and easily identified from the spectrum. Such bands exhibiting vibrational structures as those originating either from the n_0 or π_2 orbital for carboxylic acids can be directly assigned without the aid of theoretical calculations.

2. The photoelectron peak corresponding to an adiabatic ionization from the n_0 orbital is always detected and this fact implies that the n_0 orbital is almost of "non-bonding" character; the ionization from the n_0 orbital does not alter the geometry of the molecule greatly.

3. The n_0 orbital is strongly localized on the carbonyl oxygen atom. The loss of an electron from this orbital excites a $\nu_{C=O}$ vibration and weakens the C=O bond slightly. The orbital also contributes to bonding of hydroxyl hydrogen to carbonyl oxygen. It is further conceived that the orbital plays an important role in settling the carboxyl group in a molecular plane as it is, since the ionization of the n_0 orbital is accompanied by the excitation of a δ_{CH} mode in formic acid and a ρ_{COOH} mode in acetic and higher carboxylic acids.

4. The second band of carboxylic acids is verified to originate from the π_2 ionization by inspecting vibrational structures. It is found from a study of formic acid and its deuterium derivatives, that the second band has an unexpected feature, *i.e.*, the extraordinarily high frequency for the $\nu_{C=O}$ mode of the ion, and it is the case for other higher carboxylic acids, also.

Thus it is concluded that the characteristic properties of the π_2 orbital are the anti-bonding character with regard to the C=O bond, and that the π_2 orbital contributes to settling the geometrical structure of carboxyl group, since the ionization of the π_2 orbital excites only the $\nu_{C=O}$, a ν_{C-O}, and a δ_{OCO} modes which are all intrinsic vibrational modes within the carboxyl group.

5. The lack of a 0-0 peak for the second band of acetic and higher carboxylic acids corresponding to the π_2 ionization implies that the equilibrium geometry of the corresponding ions is out of the Franck-Condon region and that the ions considerably change in geometry from the neutral molecules.

References

1) C. R. Brundle, D. W. Turner, M. B. Robin, and H. Basch, *Chem. Phys. Lett.*, **3**, 292 (1969).

2) I. Watanabe, Y. Yokoyama, and S. Ikeda, This Bulletin, **46**, 1959 (1973).

3) I. Watanabe, Y. Yokoyama, and S. Ikeda, *Chem. Phys. Lett.*, **19**, 406 (1973).

4) D. A. Sweigart and D. W. Turner, *J. Amer. Chem. Soc.*, **94**, 5592 (1972).

5) R. K. Thomas, *Proc. Roy. Soc., Ser. A*, **331**, 249 (1972).

6) Y. Yokoyama, I. Watanabe, and S. Ikeda, *Bunseki Kagaku*, **20**, 1502 (1971).

7) C. V. Berney, R. L. Redington, and K. C. Lin, *J. Chem. Phys.*, **53**, 1713 (1970).

8) E. Ady and J. Brickmann, *Chem. Phys. Lett.*, **11**, 302, (1971).

9) A. Witkowski, *J. Chem. Phys.*, **52**, 4403 (1970).

10) G. L. Carlson, R. E. Witkowski, and W. G. Fateley, *Spectrochim. Acta*, **22**, 1117 (1966).

11) R. L. Redington and K. C. Lin, *J. Chem. Phys.*, **54**, 4111 (1971).

12) However, there is a possibility that the ν_{18} mode has a frequency of about a half of 310 cm^{-1}, since the frequency of 93 cm^{-1} for the ν_{18} of acetic acid has not been experimentally determined but is a theoretically predicted value. See Ref. 7.