BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(4), 958—961 (1974)

Vacuum Ultraviolet Absorption and Photoelectron Spectra of Aliphatic Ketones

Hitoshi Ogata, Jun Kitayama, Masanori Koto, Shinji Kojima, Yoshimasa Nihei, and Hitoshi Kamada

Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113

(Received December 1, 1972)

The vacuum ultraviolet absorption spectra down to 65000 cm^{-1} and HeI photoelectron spectra were measured for CH_3CHO and $RCOCH_3$ ($R=CH_3$ to t-C_4H_9). Assignments of the absorption bands are proposed with the aid of photoelectron spectra and CNDO/2 type molecular orbital calculations. Special notice has been paid to the similarity of the vibrational structure between the lowest ionization potential bands of photoelectron spectra and the second bands of vacuum ultraviolet absorption spectra.

Many experimental and theoretical studies have been made on the interpretation of the vacuum ultraviolet absorption spectra of aliphatic ketones and aldehydes.[1-8] Although some interpretation has been given, there is no agreement on the assignment of bands to electronic transitions. Recently, Lucazeau and Sandorfy measured the spectra of acetaldehyde and its deuterated homologues in the ultraviolet down to 85000 cm^{-1}, and gave detailed assignments to the individual absorption bands.[9] As for ketones, Ito *et al.* measured the spectra of aliphatic ketones, mainly methyl alkyl ketones, in the region from 50000 cm^{-1} to 60500 cm^{-1}, but they gave no definite assignment.[10] The present paper deals with the interpretation of these spectra with the aid of the photoelectron spectra (pes) of these molecules and CNDO/2 type SCF MO calculations.

Experimental

The vacuum ultraviolet absorption spectra were measured on a Jasco model VUV-2 vacuum ultraviolet self-recording spectrophotometer mounted with 1 m radius concave grating having 1200 grooves per mm, equipped with a ratio recording double beam system using the rotating-cell method. 3 cm gas cell blocks containing a sample cell and a reference cell with CaF_2 windows rotate at 8 Hz and function as a rotating sector.[11] The light sources were a hydrogen discharge tube and a zenon discharge tube. The spectra were measured in the vapor state at room temperature and recorded photoelectrically down to 65000 cm^{-1}.

A Jasco model PE-1 photoelectron spectrometer was used for measurements of the photoelectron spectra. The resonance line of He (584Å) was emitted by means of DC glow discharge. A hemispherical electrostatic condenser with 100mm diameter was used for electron energy analysis, a channel electron multiplier for detection and a pulse counting method for signal processing system. The terrestrial magnetic field and fluctuating magnetic field around the apparatus were removed by μ-metal shielding. In order to obtain ionization potentials from spectra, Xe gas was fed into the sample gas as an internal standard of ionization potential. The spectra were measured in gas phase at room temperature.

We have measured the absorption and photoelectron spectra of CH_3CHO, CH_3COCH_3, $C_2H_5COCH_3$, n-$C_3H_7COCH_3$, i-$C_3H_7COCH_3$, n-$C_4H_9COCH_3$, i-$C_4H_9COCH_3$, s-$C_4H_9COCH_3$ and t-$C_4H_9COCH_3$. These compounds were commercial products and used without further purification. Theoretical calculations were based on the CNDO/2 method.

Results and Discussion

Photoelectron Spectra. The photoelectron (pe) spectra of acetaldehyde and eight aliphatic ketones are shown in Fig. 1. Each pe spectrum of these molecules contains relatively a sharp peak located at the lowest ionization potential side (called the first band) and a series of broader peaks at the higher ionization potential region. We assume the validity of the Koopmans' theorem throughout.[12] Since the calculations have been performed in the ground state geometries, the calculated ionization potentials are compared with the experimental vertical ionization potentials throughout. Observed vertical ionization potentials and calculated ionization potentials of acetone and acetaldehyde are summarized in Table 1. For the sake of convenience,

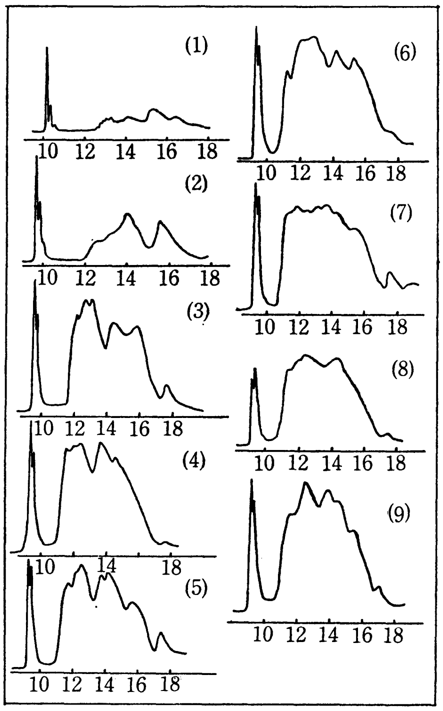

Fig. 1. The photoelectron spectra of ketones and acetaldehyde, Abscissa; ionization potential (eV). Ordinate; arbitrary unit. (1): CH_3CHO, (2): CH_3COCH_3, (3): $CH_3COC_2H_5$, (4): CH_3CO-n-C_3H_7, (5): CH_3CO-i-C_3H_7, (6): CH_3CO-n-C_4H_9, (7): CH_3CO-i-C_4H_9, (8): CH_3CO-s-C_4H_9, (9): CH_3CO-t-C_4H_9.

Table 1. Calculated and observed ionization potentials of acetone and acetaldehyde

CNDO/2		Obsd
I. P. (eV)	Symmetry	I. P. (eV)
Acetone		
13.12	$4b_2$ (n)	9.71
15.16	$2b_1$ (π)	12.62
17.06	$5a_1$ (σ)	13.70
17.62	$3b_2$ (σ)	14.18
Acetaldehyde		
13.71	7a′ (n)	10.19
16.23	2a′′ (π)	13.09
17.50	6a′ (σ)	13.93
20.86	5a′ (σ)	15.09

Table 2. The first pe bands and the second absorption bands of acetone and acetaldehyde

Acetone				
pes	peak position (eV)	9.71	9.86	10.02
	intensity (cps)	360	200	70
VUV	peak position (eV)	6.35	6.50	6.65
	intensity ($\varepsilon \times 10^{-3}$)	10.30	6.10	2.05
Acetaldehyde				
pes	peak position (eV)	10.19	10.33	10.50
	intensity (cps)	690	250	60
VUV	peak position (eV)	6.83	6.96	7.13
	intensity ($\varepsilon \times 10^{-3}$)	9.8	3.0	2.3

the types of molecular orbitals are roughly classified into n, π, and σ. The first bands of the pe spectra of acetone and acetaldehyde can be assigned to the ionization from the non-bonding orbital localized on the respective oxygen atom on the basis of their spectral features and calculated eigenvectors. The first bands of other aliphatic ketones can also be assigned to non-bonding orbitals from the same reason.

All the first bands of aliphatic ketones and aldehyde show vibrational fine structures. Peak positions and intensities of the fine structures for acetone and acetaldehyde are shown in Table 2. Three peaks can be found for acetone with spacings 0.15 and 0.16 eV and two peaks for other ketones with spacings ranging from 0.15 to 0.08 eV. In the spectrum of acetaldehyde, three peaks with spacings of 0.14 and 0.17 eV can be identified.

Results of calculations show that the second ionization bands of acetone and acetaldehyde can be assigned to the C=O π orbitals and the third bands to the C=O σ orbitals, other types of σ orbitals largely contributing to the third bands.

General Description of the VUV Spectra. The absorption spectra of acetone, first studied by Scheibe *et al.*,[13] have been investigated in detail by Lawson and Duncan,[14] Lake and Harrison,[5] and Ito *et al.*[10] Absorption spectra of acetone and acetaldehyde we obtained are shown in Fig. 2. For acetone, the absorption bands near 50000, 60000, and 65000 cm^{-1} are denoted by the second, third, and fourth absorption bands respectively, since aliphatic ketones have an absorption band near 36000 cm^{-1} assigned to the n-π^* transition. In the case of acetone, the third and fourth absorption bands are rather difficult to separate, but are separated at 62200 cm^{-1} by taking spectra of other ketones into consideration. The reproducibility of *f*-values is almost within 10 per cent and *f*-values are in fairly good agreement with those reported by Ito *et al.*,[10] except for methyl isobutyl ketone, methyl s-butyl ketone and methyl t-butyl ketone.[15] Because of overlapping with Ref. 10, the absorption spectra of aliphatic ketones are not shown except for acetone.

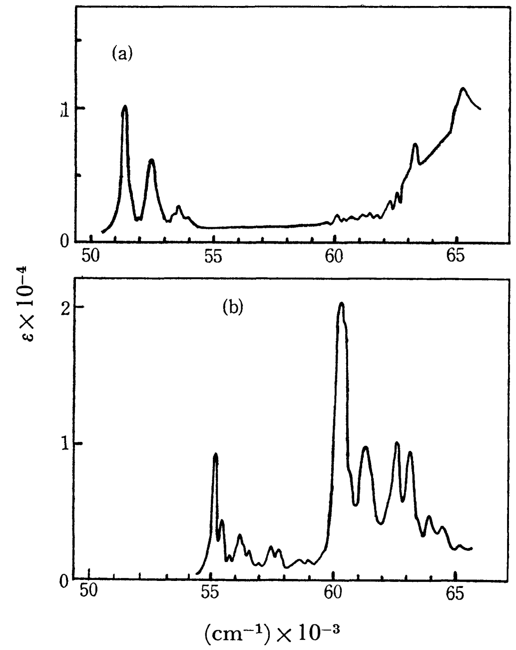

Fig. 2. The VUV absorption spectra of (a) acetone and (b) acetaldehyde.

The Second and Third Absorption Bands of Ketones. The first problem in the spectral region beyond 50000 cm^{-1} is to distinguish the Rydberg bands from the valence shell bands. Duncan[16] assigned 65000 cm^{-1} band of acetone to the Rydberg band whose quantum defect is 0.495, but its limit was not confirmed by the photoionization experiments of Watanabe,[17] who made a different assignment and obtained a series leading to an ionization potential of 9.705 eV. In contrast, Barnes and Simpson[7] assigned the weak band near 60000 cm^{-1} to the 2p-3s Rydberg transition and the strong band near 65000 cm^{-1} to the π-π^* transition. Barnes and Simpson[7] and Ito *et al.*[10] assigned the sharp peaks locating from 50000 cm^{-1} to 55000 cm^{-1} to the n-σ^* valence shell transition.

The equilibrium geometries of the excited Rydberg species and the ionic species lacking one non-bonding electron are expected to be considerably close. A similarity of the Franck-Condon factors is therefore expected between the pe spectra and optical spectra assigned to Rydberg transitions. The vibrational structure of the pe band assigned to non-bonding orbital is thought to be very much alike that of a Rydberg transition which converges into the corresponding ionization.

The fine structures of the second absorption band and of the first pe band of acetone are summarized in Table 2. As might be expected, the vibrational structure of first pe band bears a striking resemblance to that of the second absorption band. Fine structures of the second absorption bands of other ketones are considerably complicated, but the corresponding peaks can be found in the first pe bands with a few exceptions. This evidence strongly supports the assignment that the second absorption bands of aliphatic ketones are the Rydberg transitions. If we take the 51300 cm^{-1} peak of acetone for the first member of the Rydberg series and use the values obtained by Watanabe,$^{17)}$ transition energies of each absorption peak satisfy the Rydberg equation, giving the quantum defect $\delta = 1.02$. In other words, the peaks observed by Watanabe belong to the s-type Rydberg series in the range $n \geq 4$, and the 51300 cm^{-1} band is the $n=3$ Rydberg transition of the same series.

As regards the variation of the second absorption bands of aliphatic ketones by alkyl groupes, Ito *et al.* pointed out that methyl alkyl ketones could be classified into Group I, methyl *n*-alkyl ketones (including methyl isobutyl ketone) and Group II, the methyl alkyl ketones in which the α-carbons of the alkyl groups are the secondary or tertiary carbons, the shapes of these second bands being sensitive to alkyl groups.$^{10)}$ In the second bands of Group I molecules, there are main vibrational progressions with frequencies *ca.* 1200 cm^{-1}. Hardly any vibrational fine structures can be seen in Group II molecules with the exception of methyl isopropyl ketone. In particular, the difference in band shape between methyl isobutyl ketone and methyl *s*-butyl ketone is remarkable. Although the former has a fairly distinct fine structure the latter has practically no structure. This is thought to be due to the existence of conformational isomers and the characteristics of the Rydberg orbitals.

The first member of the Rydberg transition series is related to the smallest Rydberg orbitals. The first Rydberg state undergoes a larger perturbation from the molecular skelton than higher members. Because of the localization character of the lone pair orbitals, the Rydberg spectra of methyl alkyl ketones caused by the transitions from the lone pair to Rydberg orbitals are mainly affected by the structure near the carbonyl group. In the case of Group I molecules, the methyl alkyl ketones with large normal alkyl groups have essentially the same vibrational structures as methyl ethyl ketone. On the other hand, Rydberg states of Group II molecules which have branched alkyl groups at α-position are strongly perturbed by their internal rotations. In the case of methyl isobutyl ketone which has a branched alkyl group at β-position, the absorption band is considered to show several vibrational fine structures, since the Rydberg state is not much perturbed.

The vacuum ultraviolet absorption spectra of aliphatic alcohols, ROH, and amines, RNH_2 were also measured $R = (CH_3$ to $t\text{-}C_4H_9)$. Important results alone are presented here. The first electronic transition bands of ROH located at about 55500 cm^{-1} and of RNH_2 at about 47600 cm^{-1} can be assigned to the n-σ^* transitions. The variation of oscillator strengths f of the first bands of ROH and RNH_2, and the oscillator strengths of the second absorption bands of $RCOCH_3$ are shown in Fig. 3(a). The f-values of the n-σ^* bands of alcohols and those of amines undergo the same variation by alkyl substituents, the second bands of ketones showing a different tendency. Similar plots for the n-σ^* bands of alcohols and amines and for the third absorption bands of ketones are shown in Fig. 3(b). The oscillator strengths vary considerably with the alkyl group, the methyl group giving the smallest f-value and the t-butyl group the largest f-value. However, the three series of molecules show the same variation by alkyl groups.

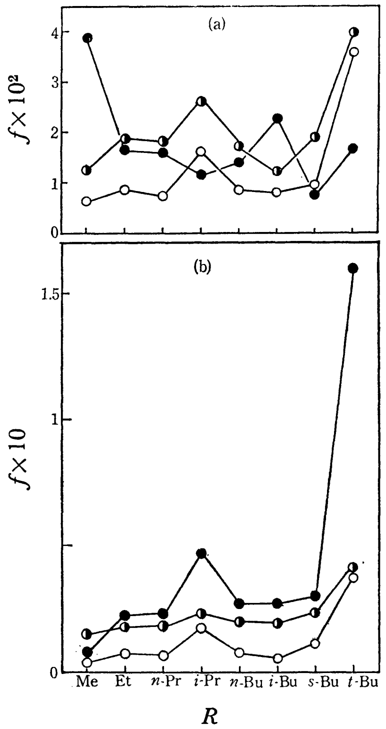

Fig. 3. The oscillator strengths of (a) the second and (b) the third absorption bands of $RCOCH_3$ and those of n-σ^* transitions of RNH_2 and ROH.
○: ROH, ◑: RNH_2, ●: $RCOCH_3$.

Taking into account the vibrational structure of the second absorption bands of ketones and the varation of the oscillator strentghs of the second and third bands, it seems reasonable to assign the second bands of ketones to the Rydberg transition and the third bands to the n-σ^* transition. The assignment is based only on experimental results, and therefore, attention should be paid to whether the lowest Rydberg orbital is distinguishable from the lowest σ^* orbital. For example, the $3sa_1$ Rydberg orbital of H_2O is identical with the antibonding orbital $4a_1$. However, in larger molecules with lower symmetry the lowest Rydberg orbital might not be identical with the lowest σ^* orbital, though mixing may occur. In this regard, the theoretical investigation by Salahub$^{18)}$ is prerequisite.

In order to obtain further proof that the second bands can be assigned to the Rydberg transition, further measurements are necessary.$^{19-21)}$ As for the second band of acetone, it was pointed out$^{19)}$ that the upper state of the transition has the characteristic of a big orbit, but the pressure effect by the use of nitrogen gas is not so extreme as methyl iodide, a well-known example. According to the assignment by Lucazeau and Sandorfy[9] acetaldehyde has the n-3s Rydberg state at 55045 cm^{-1}, the n-3p Rydberg state at 60154 cm^{-1} and the n-3d Rydberg state at 67985 cm^{-1}. Their spectra show that these peaks are very sharp and intense. In the case of acetone, on the contrary, no sharp and intense peak corresponding to n-3p or n-3d Rydberg peak of acetaldehyde can be found in this spectral region.

The Fourth Absorption Bands of Ketones. The fourth band starting at 62200 cm^{-1} could not be experimentally examined. The spectra obtained by Barnes and Simpson[7] show that this band extends to about 69000 cm^{-1} and has a large f-value. In the assignment of this band, CNDO/2 calculations were performed, orbitals with a higher principal quantum number being not included in the basis functions.

On the basis of experimental results, the third bands have been assigned to n-σ^* transitions. But CNDO/2 calculations show that the third band is π-π^* and the fourth band n-σ^*. If absorption intensities are taken into consideration and, further, from the fact that the calculated transition energies for π-π^* and n-σ^* are very close, it may not be appropriate to make direct use of calculations to assignments. The spectrum reported by Barnes and Simpson[7] shows that the f-value of the fourth band is more than ten times larger than that of the third band. Our calculations show that the f-value of π-π^* is about ten times larger than that of n-σ^*. This may support the assignment that the fourth band is the π-π^* transition.

Acetaldehyde. The first band of the pe spectrum of acetaldehyde can be assigned to the ionization from the non-bonding orbital localized on an oxygen atom. Fine structures of the first pe band and the 60000 cm^{-1} absorption band of acetaldehyde assigned to n-3s Rydberg state are summarized in Table 2. As in the case of acetone, similarity of the vibrational structure between pe and absorption spectra is recognized.

Though we could not identify it, Lucazeau and Sandorfy[9] found a very weak band in the region 53677—58254 cm^{-1} and assigned it to the n-σ^* transition on the basis of the following (1) In Rydberg series, the 0–0 component usually has maximum intensity. (2) The σ^* orbital has a conspicuous 3s Rydberg character. The f-value of this n-σ^* transition is calculated to be 0.12. This value is too large for an explanation of the weakness of this band. Our results show that the σ-π^* transition is the second transition having an f-value one tenth of the n-σ^* transition. It may thus be reasonable to assign this band to the σ-π^* rather than the n-σ^* transition, where the σ orbital has mainly CO bonding character. Calculations show that in the case of acetone the second lowest transition is also σ-π^*. In contrast with the presence of the weak band in the absorption spectrum of acetaldehyde in the region 53677—58254 cm^{-1}, no corresponding band has been found. Concerning transition energies, calculated results for acetaldehyde are consistent with the experimental results, the n-σ^* transition having lower energy than the π-π^* transition. Observed transition energies and assignments for acetone and acetaldehyde are shown in Table 3.

TABLE 3. THE OBSERVED TRANSITION ENERGIES, ΔE, AND OSCILLATOR STRENGTHS, f

Obsd		Assign.
ΔE (eV)	f	
Acetone		
4.50	4.14×10^{-4} [22]	n-π^*
6.35	3.9×10^{-2}	Rydberg
7.46	$<8.6\times10^{-3}$	n-σ^*
8.10	—	π-π^*
Acetaldehyde		
4.28	3.63×10^{-4} [22]	n-π^*
6.82	3.2×10^{-2}	Rydberg
7.46	1.8×10^{-1}	Rydberg[9]
7.75		n-σ^*[9]

References and footnotes

1) H. L. Mcmurry, *J. Chem. Phys.*, **9**, 231, 241 (1941).

2) A. D. Walsh, *Trans. Faraday Soc.*, **42**, 66 (1946).

3) W. C. Price, *J. Chem. Phys.*, **3**, 256 (1935).

4) W. C. Price, *Proc. Roy. Soc., Ser. A*, **162**, 110 (1937).

5) T. S. Lake and A. J. Harrison, *J. Chem. Phys.*, **30**, 361 (1959).

6) R. S. Holdsworth and A. B. F. Duncan, *Chem. Rev.*, **41**, 311 (1947).

7) E. E. Barnes and W. T. Simpson, *J. Chem. Phys.*, **39**, 670 (1963).

8) W. C. Johnson, Jr. and W. T. Simpson, *ibid.*, **48**, 2168 (1968).

9) G. Lucazeau and C. Sandorfy, *J. Mol. Spectrosc.*, **35**, 214 (1970).

10) H. Ito, Y. Nogata, S. Matsuzaki, and A. Kuboyama, This Bulletin, **42**, 2453 (1969).

11) Y. Nihei, S. Oda, E. Niki, and H. Kamada, *Spectrochim. Acta*, **24A**, 457 (1968).

12) T. Koopmans, *Physica*, **1**, 104 (1934).

13) G. Scheibe, F. Povenz, and C. Linstrom, *Z. Phys. Chem.*, **B20**, 283 (1933).

14) M. Lawson and A. B. F. Duncan, *J. Chem. Phys.*, **12**, 329 (1944).

15) Our experiments showed that the absorption spectra and related results of methyl isobutyl ketone and methyl *s*-butyl ketone should be named in reverse to those given in Ref. 10.

16) A. B. F. Duncan, *J. Chem. Phys.*, **3**, 131 (1935).

17) K. Watanabe, *ibid.*, **22**, 1564 (1954).

18) D. R. Salahub, *Theoret. Chim. Acta* (Berl.), **22**, 330 (1971).

19) M. B. Robin and N. A. Kuebler, *J. Mol. Spectrosc.*, **33**, 274 (1970).

20) H. Basch, M. B. Robin, N. A. Kuebler, C. Baker, and D. W. Turner, *J. Chem. Phys.*, **51**, 52 (1969).

21) J. W. Raymonda, *ibid.*, **56**, 3912 (1972).

22) E. F. Worden, *Spectrochim. Acta*, **22**, 21 (1966).