

the excitation profiles of the FeOEP complexes further suggests that these effects may be important for other C₉-substituted porphyrins, particularly ferric heme systems which exhibit relatively weak Q(0,0) absorption bands.⁴⁷ The RR studies reported here also emphasized the importance of collecting detailed profiles before attempting to interpret the trends in these data.

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(47) Makinen, M.; Chung, A. K. In "Iron Porphyrins"; Lever, A. B. P., Gray, H. B., Eds.; Addison-Wesley: Reading, MA, 1982; Part I, pp 141-235.

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Methyl- and Dimethylketene: He I Photoelectron Spectra and Vertical Ionization Potentials Calculated by Using Perturbation Corrections to Koopmans' Theorem

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He I photoelectron spectra are reported for the monomethyl and dimethyl derivatives of ketene, H₂CCO. The spectra, which beyond the first structured ionization potential show a complicated series of bands in the 12-18-eV range, have been fully assigned by using calculations employing perturbation corrections to Koopmans' theorem.

Introduction

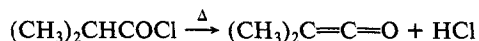
Simple derivatives of ketene are unstable with respect to dimerization or decomposition, but it has been shown by us¹⁻³ and others⁴ that it is possible to generate species of the type XHC=C=O and X₂C=C=O (X = CH₃, Cl, and Br) in the gas phase for spectroscopic observation. In most cases the technique of ultraviolet photoelectron spectroscopy (UPS) has been used to monitor the reactions, although more recently microwave and Fourier transform infrared have proved to be successful.⁵ Of the above species the monomethyl and dimethyl derivatives are by far the more stable, and consequently microwave and infrared spectra have been reported.⁶⁻⁹ However, the presence of methyl groups introduces complications into the interpretation of the photoelectron (PE) spectra, since ionization potentials (IP's) associated with the CH₃ group tend to cluster in a narrow spectral range. The accurate calculation of vertical IP's (VIP's) can go a considerable way toward solving this problem. Such results can be obtained by the method of Green's functions using large basis sets¹⁰ or, in a more cost-effective fashion, by using ordinary Rayleigh-Schrödinger perturbation theory (RSPT).¹¹ Recently,

the use of RSPT coupled with the effective core potential has provided a successful and economical method of computing VIP's for the monochloro- and dichloroketenes.¹²

In this work we employ ordinary third-order RSPT to provide an analysis of the complicated PE spectra of the monomethyl- and dimethylketenes.

Experimental Section

Methyl- and dimethylketene were prepared by low-pressure gas-phase pyrolysis (700-750 °C) of respectively propanoyl chloride and 2-methylpropanoyl chloride in a 120 mm × 7 mm i.d. quartz tube. The reaction, which involves a dehydrochlorination, can be represented for dimethylketene by



HCl was removed by gas-phase titration with NH₃ and the effluent from the reaction was led directly into the ionization chamber of a photoelectron spectrometer.¹³ As illustrated by the PE spectra, this is an efficient route, giving virtually pure ketenes. Spectra were calibrated with the known IP's of CH₃I, CO, N₂, and Ar.

Computational Details

The geometry of methylketene and dimethylketene was taken from ref 7 and 9, respectively. For basis functions, a standard double- ζ (DZ) set was used. It consists of Huzinaga's (9s5p;4s) Cartesian Gaussian functions¹⁴ contracted to (4s2p;2s) with Dunning's coefficients.¹⁵ The hydrogen orbitals were scaled by the usual factor of 1.2.

(1) D. Colbourne, Ph.D. Thesis, University of British Columbia, 1979.

(2) D. Colbourne, D. C. Frost, C. A. McDowell, and N. P. C. Westwood, *J. Chem. Soc., Chem. Commun.*, 250 (1980).

(3) D. Colbourne et al., to be submitted for publication.

(4) H. Bock, T. Hirabayashi, and S. Mohmand, *Chem. Ber.*, **114**, 2595 (1981).

(5) M. C. L. Gerry, W. Lewis-Bevan, and N. P. C. Westwood, *J. Chem. Phys.*, **79**, 4655 (1983).

(6) B. Bak, D. Christensen, J. Christiansen, L. Hansen-Nygaard, and J. Rastrup-Andersen, *Spectrochim. Acta*, **18**, 1421 (1962).

(7) B. Bak, J. J. Christiansen, K. Kuntmann, L. Nygaard, and J. Rastrup-Andersen, *J. Chem. Phys.*, **45**, 883 (1966).

(8) W. H. Fletcher and W. B. Barish, *Spectrochim. Acta*, **21**, 1647 (1965).

(9) K. P. R. Nair, H. D. Rudolph, and H. Dreizler, *J. Mol. Spectrosc.*, **48**, 571 (1973).

(10) W. von Niessen, G. H. F. Diercks, and L. S. Cederbaum, *J. Chem. Phys.*, **67**, 4124 (1977), and references therein.

(11) D. P. Chong and S. R. Langhoff, *Chem. Phys.*, **67**, 153 (1982).

(12) S. R. Langhoff and D. P. Chong, *Chem. Phys. Lett.*, **100**, 259 (1983).

(13) D. C. Frost, S. T. Lee, C. A. McDowell, and N. P. C. Westwood, *J. Electron Spectrosc. Relat. Phenom.*, **12**, 95 (1977).

(14) S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965).

(15) T. H. Dunning, Jr., *J. Chem. Phys.*, **53**, 2823 (1970).

TABLE I: Vertical Ionization Potentials (in eV) of Methylketene

MO	obsd ^a	av GA	ΔE^{GA}	KT
3a''	8.92 ^b	8.52	8.54	9.46
12a'	13.29	12.94	12.97	14.44
11a'	13.72	13.56	13.59	15.09
2a''	14.11	14.15	14.18	15.69
1a''	15.22	14.63	14.74	17.63
10a'	15.55	15.02	15.08	16.90
9a'	16.63	16.39	16.47	18.61
8a'	17.61	17.45	17.67	20.01
av abs dev	(0)	0.31	0.26	1.60
max abs dev	(0)	0.59	0.48	2.41

^a First IP ± 0.02 eV; remaining IP's ± 0.05 eV. ^b Vibrational structure, 1130 and 2180 $\text{cm}^{-1} \pm 40 \text{ cm}^{-1}$.

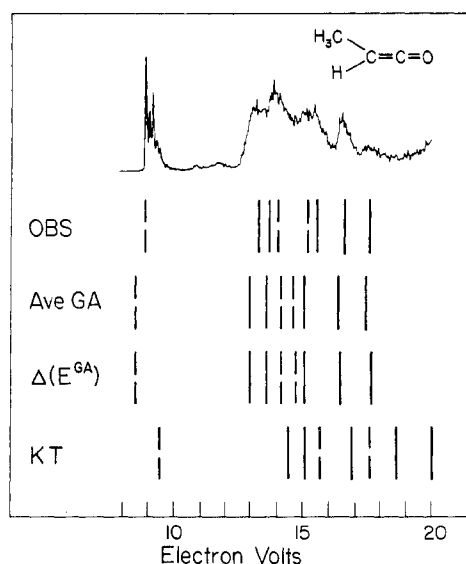


Figure 1. Summary of observed and calculated vertical ionization potentials of methylketene. Bars with break indicate ionization from a'' (π) orbitals.

The vertical ionization potentials were calculated by the method of perturbation corrections to Koopmans' theorem (KT).^{11,16,17} From past experience,^{11,18} the best estimates of vertical ionization potentials are provided by the average of our two previous geometric approximations¹⁶ when larger basis sets are used. But for smaller sets such as 4-31G and DZ, the use of ΔE^{GA} was recommended.¹¹ Both estimates are reported in the following sections.

To keep the computing costs down, no excitations were permitted from any core orbitals. In addition, two innermost valence molecular orbitals were kept doubly occupied in all configurations in all of the calculations on methylketene. Then, for each parent molecule or cation, we include all single excitations from a single-configuration reference plus a subset of double excitations with coefficients greater than a selected threshold value of 0.01 (subject to the restriction of doubly occupied low-lying molecular orbitals). The use of such severe truncation of the molecular orbital space and of the first-order wave functions was based on our recent experience with similar calculations on chloroketene and dichloroketene.¹²

Assignments

Although the He I photoelectron spectra of methyl- and dimethylketene have been reported previously,^{1,4} a full assignment has not been attempted.

Methylketene. The observed and calculated VIP's and the proposed assignments are shown in Table I and Figure 1. The

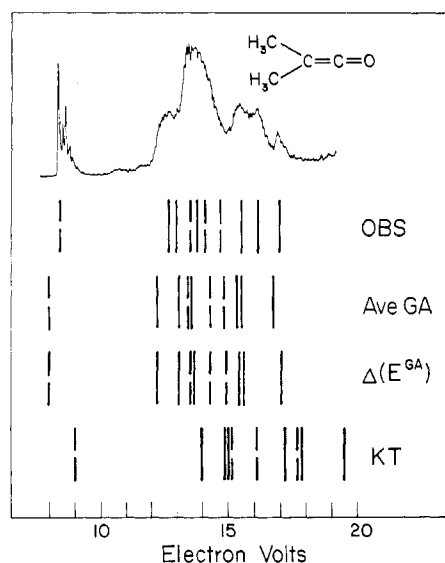


Figure 2. Summary of observed and calculated vertical ionization potentials of dimethylketene. Bars with break indicate ionization from b₁ (π) and a₂ (π) orbitals.

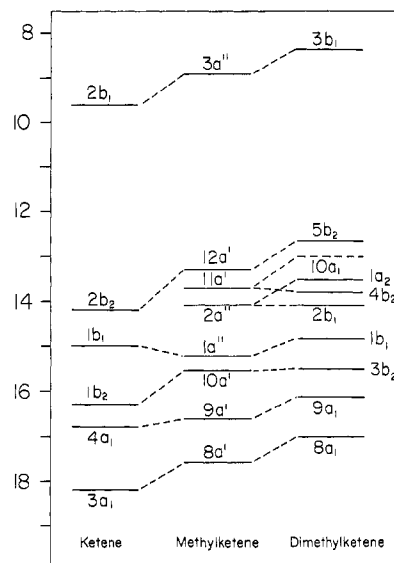


Figure 3. Correlation diagram for the experimental IP's of ketene, methylketene, and dimethylketene.

first distinct IP (8.92 eV) which is characteristic of all ketenes corresponds to an out-of-plane π nonbonding orbital (a'' in C_s symmetry) and shows resolvable vibrational structure. The observed frequencies of 1130 and 2180 cm^{-1} in the ion correspond to excitation of the C=C and C=O vibrational modes, respectively, and although molecular ground-state frequencies are not known, they should be close to those for dimethylketene (1392 and 2134 cm^{-1}).⁸ This would imply that this orbital is C=C bonding and C=O antibonding, in accord with the calculations.

Beyond 12.5 eV individual IP's are partially overlapped, and recourse to the RSPT calculations is required to satisfactorily interpret the spectrum. Two distinct IP's at 16.63 and 17.61 eV can be readily assigned to orbitals of a' symmetry as shown in Table I and Figure 1 and are in excellent agreement with the calculations. Of the eight observable IP's in the He I range, the five remaining are assigned according to the calculations as shown in the Table I and Figure 1. The distribution of a' and a'' orbitals follows smoothly from the assignment of the parent ketene molecule,^{19,20} as shown in the correlation diagram of Figure 3.

(16) D. P. Chong, F. G. Herring, and D. McWilliams, *J. Chem. Phys.*, **61**, 78, 958, 3567 (1974).

(17) D. P. Chong and Y. Takahata, *Int. J. Quant. Chem.*, **12**, 549 (1977).

(18) S. R. Langhoff and D. P. Chong, *Chem. Phys. Lett.*, **86**, 487 (1982).

(19) D. Hall, J. P. Maier, and P. Rosmus, *Chem. Phys.*, **24**, 373 (1977).

(20) D. P. Chong, *Theor. Chim. Acta*, **50**, 181 (1978).

TABLE II: Vertical Ionization Potentials (in eV) of Dimethylketene

MO	obsd ^a	av GA	ΔE^{GA}	KT
3b ₁	8.38 ^b	7.97	8.00	8.95
5b ₂	12.67	12.20	12.23	13.93
10a ₁	13.0	13.09	13.09	14.95
1a ₂	13.52	13.52	13.51	15.12
4b ₂	13.8	13.60	13.65	15.05
2b ₁	14.1	14.28	14.35	16.10
1b ₁	14.8	14.81	14.95	17.66
3b ₂	15.50	15.34	15.40	17.18
9a ₁	16.15	15.54	15.59	17.86
8a ₁	17.03	16.74	17.08	19.50
av abs dev	(0)	0.24	0.22	1.74
max abs dev	(0)	0.61	0.56	2.86

^a First IP \pm 0.02 eV; remaining IP's \pm 0.05 eV unless otherwise specified. ^b Vibrational structure, 1260 and 2180 cm⁻¹ \pm 40 cm⁻¹.

All orbitals are destabilized, as expected, except for the ketene 1b₁ π bonding orbital, which is slightly stabilized in methylketene (1a'') due to bonding H 1s contributions and a resonance interaction with the 2a'' orbital.

Dimethylketene. Addition of another CH₃ group introduces a further two orbitals (one in and one out of plane) into the 13-14-eV region, for a total of ten orbitals in the He I range.

The first IP at 8.38 eV is again distinctive, showing two resolvable progressions of 1260 and 2180 cm⁻¹, corresponding to the C=C ($\nu_{\text{mol}} = 1392$ cm⁻¹) and C=O ($\nu_{\text{mol}} = 2134$ cm⁻¹)⁸ stretching frequencies. This band is assigned to the out-of-plane π nonbonding orbital (3b₁ in C_{2v} symmetry). The broad band at 12.67 eV follows the in-plane nonbonding orbitals of ketene and methylketene and is therefore assigned to the 5b₂ orbital. Between

13 and 15 eV the density of orbitals is high, but nevertheless five IP's can be assigned to the molecular orbitals 10a₁, 1a₂, 4b₂, 2b₁, and 1b₁, following the calculations as shown in Table II and Figure 2. The experimental spread of these five orbitals is 1.8 eV; the calculated (average GA) spread is 1.72 eV. The remaining three distinct IP's from 15-17 eV can then be assigned to the 3b₂, 9a₁, and 8a₁ orbitals.

Discussion

Although the numerical agreement with the calculated IP's is good, as exemplified by the deviations shown in Tables I and II, and the trends in Figure 3 are generally smooth, there is a minor query concerning the relative positions of the 1b₁ and 3b₂ orbitals of dimethylketene. Virtually all orbitals are destabilized with introduction of the second CH₃ group, although the 1b₁ orbital is predicted to be stabilized relative to the 1a'' orbital of methylketene. It is conceivable, therefore, that a switch of these two orbitals could occur, in contrast to the calculated results although this would require an unacceptably large shift of the calculated values. To investigate this possibility, the threshold value of 0.01 was reduced to 0.005; the 1b₁ to 3b₂ separation was only slightly affected (from 0.53 to 0.47 eV). Moreover, addition of polarization functions on all the atoms changed the Koopmans' estimate of the 1b₁ to 3b₂ separation by only 0.02 eV. These additional calculations therefore support the present ordering. Apart from the dense CH₃ region (13-14 eV) this assignment then parallels that for dichloroketene.¹²

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Nonergodic Behavior, Possibly due to an Insufficient Density of States, in the Decompositions of $\dot{\text{C}}\text{H}_2\text{C}(\text{OH})\text{OD}^+$

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The metastable $\dot{\text{C}}\text{H}_2\text{C}(\text{OH})\text{OD}^+$ ion loses OH and CH₂D via $\text{CH}_2\text{DCO}_2\text{H}^+$ and CH₃ and OD via $\text{CH}_3\text{CO}_2\text{D}^+$. About 3.7 kJ mol⁻¹ (ca. 45%) more energy is released in the loss of OH than in the loss of OD, and less energy is released in the loss of CH₂D than of CH₃. The differing energy releases cannot be accounted for by isotopic influences on zero-point energies. It is concluded that energy is deposited differently in the intermediate acetic acid ions depending on whether H or D is transferred and that this difference is maintained and reflected in the subsequent fragmentations. Energy may remain localized because the fragmenting ions do not contain enough energy for the density of states to be high enough to permit energy randomization between isomerization and decomposition.

Introduction

Recently Holmes and Lossing¹ reported the interesting observation that the O-deuterated enol isomer of the acetic acid ion (1-O-d) released 1.5 times as much translational energy upon losing OH as upon losing OD. They proposed that the greater energy release resulted from the selective suppression of the lower energy of two reactions, one stepwise and one concerted (Scheme I), when D rather than H is transferred from oxygen to carbon.

Others have concluded that 1 isomerizes to 2 and decomposes in a stepwise fashion.^{2,3} Proposed decompositions of 1-O-d at 10⁻⁶-10⁻⁵ s following its formation are summarized in Scheme I.

OD is lost about three times as frequently as OH from 1-O-d.¹⁻³ This isotope effect on the relative intensities of the OH and OD losses is about what would be expected if only one reaction were

(1) Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* **1980**, *102*, 3732.

(2) Schwarz, H.; Williams, D. H.; Wesdemiotis, C. *J. Am. Chem. Soc.* **1978**, *100*, 7052.

(3) Griffin, L. L.; McAdoo, D. J. *J. Phys. Chem.* **1979**, *83*, 1142.