PHYSICAL REVIEW A VOLUME 11, NUMBER 5 MAY 1975

Theoretical analysis of the Auger spectra of CH_4

I. B. Ortenburger and P. S. Bagus
IBM Research Laboratory, San Jose, California 95193
(Received 13 January 1975)

Self-consistent-field wave functions and energies have been used to obtain an interpretation of the *KLL* Auger spectra of CH_4. The computed Auger energies are in good agreement with observed values. The multiplet structure and splittings of the final states of CH_4^{+2} are shown to play a key role in determining the spectra. For the first time, symmetry assignments have been made for the final states of the Auger transition peaks in a molecule.

I. INTRODUCTION

In an Auger transition an initial state which has a core hole decays to a final state where one electron has dropped from a higher level to fill the core hole and a second electron is ejected from the system.[1] Thus the final state of the transition is (at least) a doubly positive ion; the kinetic energy of the ejected electron gives the difference in energy between the initial and final states. The final state will very often have an open-shell configuration which will give rise to several multiplets (described by L-S or J-J coupling as appropriate). The resulting multiplet structure in atomic Auger spectra has been observed[2] and explained rather successfully theoretically using one-electron theory.[3]

In this paper, we report the first theoretical analysis of the Auger spectra of a vapor-phase molecule. Our analysis of the CH_4 spectra is obtained using extended basis-set Hartree-Fock self-consistent-field (SCF) wave functions and energies. The SCF wave functions have been calculated separately for the initial carbon 1s-hole state and all appropriate final double ion configurations and multiplets so that relaxation effects[3,4] have been taken fully into account.

Recently, the experimental Auger spectra has been reported[2(b),5] as four lines with the most intense line having the rather large width [full width at half-maximum (FWHM)] of 6 eV. In molecular spectra, linewidths may be broadened because of unresolved structure due to transitions between the vibrational levels of the initial and final states. In particular, if the potential surface (or an appropriate region of the surface) of one of the states is strongly repulsive the line can be broadened considerably. In fact, the 6-eV width of the 250-eV Auger transition in CH_4 has been ascribed[2(b),5] to the rapid dissociation of CH_4^{2+} to $CH_3^+ + H^+$.

However, our theoretical results show that unresolved multiplet structure of the four multiplets of CH_4^{+2} in the configuration $1a_1^2 2a_1^2 1t_2^4$ will contribute significantly to the large observed width of this transition.

Our theoretical results are in excellent agreement with both relative and absolute experimental Auger transition energies. Thus, we are able to make the first theoretical assignment of a rather complex molecular Auger spectra.

II. COMPUTATIONAL DETAILS

The SCF calculations were performed using a large basis set of contracted Gaussian-type (CGTO) basis functions. For carbon, 12s, 7p, and 2d elementary Gaussians were contracted to 8s, 5p, and 2d CGTO's; for H 6s and 2p functions were contracted to 5s and 2p CGTO's. The exponents for this basis set were kindly supplied to us by Pacansky.[6]

The SCF energy for the ground state is −40.214 834 hartrees for $r(\mathrm{CH}) = 2.066$ bohrs which is very nearly the SCF equilibrium geometry.[7] To our knowledge this is the lowest energy reported for CH_4; the previous lowest value[8] is $E = -40.214\,178$ hartrees for $r(\mathrm{CH}) = 2.05$ bohrs. The parameters of the basis set are given in Table I. The basis is quite large and only the functions with the largest exponents were contracted. Thus, this basis set should also be able to describe the ionic states of CH_4^+ and CH_4^{+2}, of interest for the Auger transitions, quite well. In order to examine the dependence of the Auger transition energies on basis-set size and to prepare for studies of larger molecules, the SCF wave functions were also computed using a smaller basis set. This smaller set consists of 6s, 4p, and 1d CGTO's on C and 4s and 1p on H.

All wave functions have been computed for $r(\mathrm{CH}) = 2.066$ bohrs and in a tetrahedral geometry. All transition energies, including ionization potentials and Auger electron kinetic energies, have been obtained by taking differences of the SCF total energies of the initial and final electronic states

TABLE I. Contracted Gaussian basis set.

	Exponent	Coefficient
C *s*	27 740.0	0.000 117 0
	4144.0	0.000 912 0
	939.5	0.004 787
	264.8	0.019 86
	85.78	0.067 68
	30.67	0.1821
	11.82	1.0
	4.867	1.0
	2.097	1.0
	0.6781	1.0
	0.2630	1.0
	0.1026	1.0
C *p*	51.72	0.002 734
	12.34	0.018 98
	3.772	0.080 81
	1.325	0.2278
	0.5055	1.0
	0.1983	1.0
	0.077 31	1.0
C *d*	1.200	1.0
	0.200	1.0
H *s*	82.64	0.002 006
	12.41	0.015 35
	2.824	1.0
	0.7977	1.0
	0.2581	1.0
	0.089 89	1.0
H *p*	1.100	1.0
	0.200	1.0

of the process. The wave functions and energies have been separately optimized for all states of interest. These transition energies correspond to vertical transitions but with electronic relaxation effects[3,4] taken into account.

The molecular orbitals, MO's, were constrained to have symmetry appropriate to the T_d point group. However, MO's belonging to a degenerate representation (the $1t_2$ shell in our case) were not always required to transform exactly into each other under group operations. That is, although the symmetry restriction was always maintained, the equivalence restriction was not.[9]

All wave-function calculations were performed using the joint MOLECULE/ALCHEMY SCF program.[10]

III. RESULTS AND DISCUSSION

The computed total energy of the ground state is −40.2148 hartrees. The K-shell ionization potential is 290.88 eV, which is in excellent agreement with the ESCA (electron spectroscopy for chemical analysis) measurement of 290.7 ± 0.7 eV.[2]

Methane has symmetry T_d and the ground state consists of filled shells in the configuration $1a_1^2 2a_1^2 1t_2^6$ with total symmetry $^1A_1$. The K-shell hole configuration of CH_4^+, the initial state of the Auger process, is $1a_1^1 2a_1^2 1t_2^6 (^2A_1)$. The doubly ionized final-state configurations can be either $1a_1^2 1t_2^6$, $1a_1^2 2a_1^1 1t_2^5$, or $1a_1^2 2a_2^2 1t_2^4$. The first configuration can couple only to $^1A_1$. The second configuration is split into a singlet and a triplet: $^1T_2$ and $^3T_2$. Finally, the third configuration[11] contains one triplet, $^3T_1$, and three singlets; ^1E, $^1T_2$, and $^1A_1$.

The excited states and the kinetic energies of the Auger electrons are given in Table II. In our interpretation of the experimental spectrum the $^1T_2$-$^3T_2$ splitting accounts for the second and third observed lines. The broad (6-eV half-width) fourth peak, from which the third is barely resolved, is made up of four lines. In Table III we give the final-state energies relative to the ground state, with the energy of the highest ($^1A_1$) level adjusted to the experimental value. Here we see that the agreement of the adjusted final-state energies with experiment is excellent, in all cases falling within experimental error.

The absolute energies of the Auger transition energies are in very good agreement with experiment. However, the relative energies of the various Auger final states (cf., Table III) are in even better agreement. This good agreement for the Auger level energies lends extremely strong support to our assignment of the symmetries of the final states of CH_4^{+2}.

The Auger energies obtained using the small C ⟨6s, 4p, 1d⟩ and H ⟨4s, 1p⟩ CGTO basis set were nearly identical to the results discussed above for the large C ⟨8s, 5p, 2d⟩ and H ⟨5s, 2p⟩ basis set. The differences in the Auger electron kinetic energies were less than 0.1 eV; for the relative energies, they were less than 0.01 eV.

In order to discuss intensities of the Auger transitions, it is convenient to describe the transition as

$$\phi_{i\lambda}^I \phi_{j\mu}^I \rightarrow \phi_{1a_1}^F \epsilon\lambda^F . \qquad (1)$$

Here the ϕ^I represent bound MO's in shells $i\lambda$ and $j\mu$ of the K-shell hole state of CH_4^+; $\phi_{1a_1}^F$ is the final state, doubly filled, $1a_1$ MO, and $\epsilon\lambda^F$ the MO of the continuum ejected electron. The symmetry of this ejected electron is such that the total symmetry of CH_4^{+2} and $\epsilon\lambda^F$ is $^2A_1$, the same as the symmetry of the initial K-shell hole state. Let us consider, for simplicity, that the MO's of the initial and final states are orthogonal to each other, i.e., no electronic relaxation. Then the Auger transition probability, W_a, is given by

TABLE II. Calculated and experimental Auger electron kinetic energies in eV for methane. The calculated ground-state energy of CH_4 is −40.2148 hartrees and the K-shell ionization potential is 290.88 eV.

CH_4^{++}		Theory	Expt.[a]
$1a_1^2 1t_2^6$	$^1A_1$	230.43	229.4 ± 0.4
$1a_1^2 2a_1 1t_2^5$	$^1T_2$	238.64	237.0 ± 1.0
	$^3T_2$	244.96	243.3 ± 1.5
$1a_1^2 2a_1^2 1t_2^4$	$^1A_1$	249.26	250.0 ± 0.3
	$^1T_2$	251.72	
	^1E	253.66	
	$^3T_1$	254.70	

[a] See Refs. 2(b) and 5.

$$W^a = (2\pi/\hbar)|A(\phi_{i\lambda}^I \phi_{j\mu}^I | \phi_{1a_1}^F \epsilon\lambda^F) + B(\phi_{i\lambda}^I \phi_{j\mu}^I | \epsilon\lambda^F \phi_{1a_1}^F)|^2 , \qquad (2)$$

where the integral $(ab|cd)$ is defined as

$$(ab|cd) = \int a(1) b(2) e^2_{r_{12}} c(1) d(2)\, dr_1\, dr_2 . \qquad (3)$$

The coefficients A and B are determined from considerations of symmetry. Without some estimate of the continuum orbital, $\epsilon\lambda$, we cannot make an estimate of W_a. However, from the group theoretic properties of the T_d point group,[11] we *can* say that W_a, for each of the transitions considered here, will not be zero.

TABLE III. Adjusted energies of the Auger states of methane in eV.

CH_4^{++}	Theory	Expt.[a]
$^1A_1$	61.4 adjusted	61.4 ± 0.8
$^1T_2$	53.19	53.8 ± 1.2
$^3T_2$	46.86	47.3 ± 1.2
$^1A_1$	42.57	40.7 ± 0.8
$^1T_2$	40.11	
^1E	38.17	
$^3T_1$	37.13	

[a] See Refs. 2(b) and 5.

IV. CONCLUSIONS

We have reported for the first time a theoretical analysis of the Auger spectra of a molecule. The computed transition energies are in very good agreement with experiment; so good, in fact, that an unambiguous assignment of configuration and symmetry can be made for the final state of CH_4^{+2} for each of the observed Auger peaks. It is clear from our results that the multiplet splittings of the final states plays an important role in the interpretation of observed spectra.

On the basis of our results, it is reasonable to expect that SCF wave functions can provide a basis for the quantitative interpretation of molecular Auger spectra.

---

[1] For a detailed description of the Auger process see, for example, E. H. S. Burhop and W. N. Asaad, in *Advances in Atomic and Molecular Physics*, edited by D. R. Bates and I. Esterman (Academic, New York, 1972), Vol. 8.

[2] See, for example, (a) K. D. Sevier, *Low-Energy Electron Spectrometry* (Wiley, New York, 1972); (b) K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. E. Heden, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, *ESCA Applied to Free Molecules* (North-Holland, Amsterdam, 1969).

[3] D. A. Shirley, Phys. Rev. 7, 1520 (1973).

[4] P. S. Bagus, Phys. Rev. 139, A619 (1965).

[5] R. Spohr, T. Bergmark, N. Magnusson, L. O. Werme, C. Nordling, and K. Siegbahn, Physica Scripta 2, 31 (1970).

[6] J. Pacansky (private communication). The basis-set exponents were chosen using results from atomic SCF calculations by F. B. van Duijneveldt (IBM Research Report No. RJ 945 (1971) (unpublished) and molecular SCF calculations on CH_4 cited in Refs. 7 and 8.

[7] E. Clementi and H. Popkie, J. Am. Chem. Soc. 94, 4057 (1972).

[8] W. Meyer, J. Chem. Phys. 58, 1017 (1973).

[9] R. K. Nesbet, Proc. R. Soc. Lond. A230, 312 (1955).

[10] The joint MOLECULE-ALCHEMY program package incorporates the MOLECULE integral program and the ALCHEMY SCF program. MOLECULE was written by Dr. J. Almlöf of the University of Uppsala, Sweden. The ALCHEMY SCF program was written by one of us (P.S.B.) and B. Liu of the IBM San Jose Research Laboratory. The interfacing of these programs was performed by Dr. U. Wahlgren (presently at the University of Uppsala) and P.S.B. at IBM. For a description of MOLECULE see J. Almlöf, Proceedings of the Second Seminar on Computational Problems in Quantum Chemistry, Strassburg, 1972 (Max-Planck-Institut, Munchen, 1973), p. 14 (unpublished). For a description of the ALCHEMY-SCF program see P. S. Bagus, IBM Research Report No. RJ 1077 (1972) (unpublished).

[11] See any standard text on group theory, for example, F. A. Cotton, *Chemical Applications of Group Theory* (Wiley, New York, 1971).