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Electron Impact Spectra of Some Saturated Hydrocarbons*

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Abstract

Energy-loss spectra are reported for methane, ethane, propane, n-butane, n-pentane, 2-methylpentane, 2,3-dimethylbutane and cyclohexane at a scattering angle of 0° and electron impact energy of 50 ev. Where comparisons are available with spectra obtained at higher impact energies there appears no evidence for appreciable energy dependence. Additionally the 50 ev spectra when appropriately corrected as suggested by the Born approximation agree well with optical spectra. A shoulder on the low-energy side of the first major peak of ethane, propane, n-butane and n-pentane shifts with increasing number of alkane carbon atoms as do the first three peaks and is attributed to a predominantly C-C excitation. Nothing additional in the spectra of the non-cyclic hydrocarbons has been found in the region from 2 to 7 ev.

I. Introduction

In May 1974 the 0° analyzer of our electron impact spectrometer began to operate at a performance level reasonably close to what had been predicted on the basis of its design parameters. For a 50 ev beam energy we achieved a zero energy loss ($\Delta E = 0$) current at the Faraday cup detector of 1.8×10^{-9} amp with a full width at half maximum of 125 mv and beam current reduction of $\approx 5 \times 10^5$ at an analyzer setting $\Delta E = 2$ ev. With both N_2 and He in the scattering chamber, the energy loss scale was found to agree with published spectra to ± 0.05 ev and intensity ratios of the allowed transitions agreed to within 10%. For the purpose of surveying 0° spectra of saturated hydrocarbons, this performance was considered adequate and accordingly we present in this report preliminary results on methane, ethane, propane, butane, pentane, 2-methylpentane, 2,3-dimethylbutane and cyclohexane. A study of other compounds is in progress.

II. Results and Discussion

In Fig. 1 we present typical recorded energy-loss spectra of propane and cyclohexane for electrons of 50 ev and at a scattering angle of 0° ($\pm 0.8^\circ$). In Figs. 2 and 3 composite spectra are presented of all compounds studied in order to more conveniently indicate changes with molecular structure. Although we have not yet made systematic studies of the hydrocarbons at primary energies above 50 ev, a comparison of our methane spectrum with those obtained by others at higher energies is presented in Table I and it appears that, at least for methane, there is little evidence

as yet for appreciable alteration in the spectra from 50-500 ev. The
(2) somewhat higher relative intensities obtained by Huebner¹ and by Lassetre²
at the larger energy losses (ΔE) may perhaps be a consequence of differences
in acceptance angle since indeed this is the direction in which the intensities
(2,3) change as the scattering angle increases.^{2,3}

Another indication of the insensitivity of the 50 ev spectra to further
increase in primary energy is obtained by comparison with the optical spectra.
Assuming the validity of the Born approximation to 50 ev, the electron impact
intensity at an energy loss ΔE when multiplied by $(\Delta E)^3$ is expected to
(4) be proportional to the optical extinction coefficient.⁴ This indeed is
verified for all of our impact spectra when compared to the optical measure-
(5) ments of Raymonda and Simpson.⁵ In Fig. 4 an example of such a comparison
is presented for 2,3-dimethylbutane.

With the exception of methane, all other n -alkane spectra thus far
studied exhibit a weak shoulder on the low energy side of the first main
energy loss. This can be seen to some extent in Figs. 1-3 but is made
more apparent in Fig. 5 which shows a recorded ethane spectrum at higher
sensitivity. To check the reality of this feature, we have plotted in
Fig. 6 the energy-loss position of the shoulder together with the positions
of the first three major peaks as a function of number of carbon atoms,
 N_C . The similarity in behavior of all four energy losses is obvious and
assignment to a predominantly C-C excitation is suggested by the fact that
the $N_C = 1$ extrapolated values of ΔE do not at all coincide with observed
methane energy losses. A similar shoulder is found in cyclohexane at
 ~ 8 ev (approximately its predicted position for $N_C = 6$) and at a somewhat

(o)(2)

Lower energy ~ 7.7 ev for 2-methylpentane. Since these features also appear in 400^6 and 500^2 ev n-alkane spectra it is unlikely that they have significant contribution from an exchange amplitude.

Thus far we have found no evidence in forward scattering at 50 ev for any real energy loss in non-cyclic hydrocarbons between 2 and 7 ev other than could be attributed to residual impurities. If there are, in fact, such losses in this region, their cross-section is estimated to be not larger than 5% of the first major peak. For cyclohexane a weak loss at 5 ev is being further studied.

Additional work on other saturated hydrocarbons is in progress as well as an extension to lower impact energies and larger scattering angles. Also optical spectra are being obtained in the region from 4-9 ev for better comparison with the energy loss measurements.

Acknowledgements

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Table I. Comparison of methane impact spectrum for primary energies from 50-500 ev.

energy loss (ev)	Relative Intensity ^a				
	50 ev ^b	100 ev ^c	100 ev ^d	400 ev ^e	500 ev ^f
9.71	1.00	1.00	1.00	1.00	1.00
10.35	0.93	0.88	0.87	0.88	0.88
11.59	0.96	0.99	0.92	0.92	1.00
12.80	0.90	1.06	0.94	0.92	1.07
13.30	0.84	1.09	0.90	0.90	1.14

^a Normalized to unity at 9.71 ev.

^b This work.

^c Reference 1.

^d E. N. Lassettre, A. Skerbele and M. A. Dillon, J. Chem. Phys. 49, 2382 (1968).

^e Reference 6.

^f Reference 2.

References and Footnotes

- * This research has been supported in part by the Graduate School of the University of Minnesota and in part by the U. S. Atomic Energy Commission (Document No. C00-913-58).
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 4. In our case, correction for the finiteness of the acceptance angle was negligible.
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Figure Captions

- Fig. 1. Recorded electron-impact spectra of (A) propane and (B) cyclohexane at 50 ev and 0° scattering angle.
- Fig. 2. Composite electron-impact spectra of (A) methane, (B) ethane, (C) propane, (D) n-butane and (E) n-pentane at 50 ev and 0° scattering angle.
- Fig. 3. Composite electron-impact spectra of (A) 2-methylpentane, (B) 2,3-dimethylbutane and (C) cyclohexane.
- Fig. 4. Oscillator strength density (in arbitrary units) for 2,3-dimethylbutane from 50 ev electron-impact data (O) and Raymond and Simpson's⁵ optical data (●).
- Fig. 5. Recorded electron-impact spectrum of ethane at 50 ev and 0° scattering angle showing shoulder at 8.5 ev.
- Fig. 6. Plot of the 50 ev, 0° angle energy-loss positions, ΔE , of (A) shoulder, (B) first peak, (C) second peak and (D) third peak of n-alkanes as function of number of carbon atoms, N_C .

Fig. 1.

Fig. 2.

Fig. 3.

10

OSCILLATOR STRENGTH DENSITY (arbitrary units)

5

0

7

8

9

10

11

12

ENERGY LOSS (eV)

Fig. 4.

Fig. 5.

Fig. 6.