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Infrared Spectra of Isotopically Labeled Compounds. I. Diisopropylketones

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The infrared spectra of isotopically labeled diisopropylketones were investigated. The 1712 cm.$^{-1}$ carbonyl frequency of diisopropylketone is shifted to 1675 cm.$^{-1}$ upon C^{13} substitution in the carbonyl group, and to 1681 cm.$^{-1}$ upon O^{18} substitution, indicating that it is composed of C=O and C—C stretches, in agreement with Halford's treatment of the carbonyl force constant for unconjugated ketones. The same carbonyl shift, 37 cm.$^{-1}$, is observed in the spectra of 2-methylpropionic-1-C^{13} and 2,2-dimethylpropionic-1-C^{13} acids. The 1024 cm.$^{-1}$ frequency of the ketone, shifted to 1004 cm.$^{-1}$ upon C^{13} substitution, and unaffected by either O^{18} or deuterium substitutions in the molecule, is assigned to an uncoupled C—C—C stretching vibration. The 1203 cm.$^{-1}$ frequency is assigned to C=O, C—C, and C—H coupled vibrations. Three other frequencies, 1129 cm.$^{-1}$, 983 cm.$^{-1}$, and 858 cm.$^{-1}$ are skeletal vibrations without any C—O contribution.

Studies of isotope shifts, caused by either C^{13} or C^{14}, in elucidating the infrared spectra of organic compounds are practically absent from the literature. Most of the studies published relate either to elements or to simple inorganic molecules.[2,3] Isotope shifts in simple organic compounds, caused by C^{13} of natural abundance, have been observed in the Raman spectra and quantitatively reported in the literature.[4,5]

The infrared spectrum of 2,4-dimethyl-3-pentanone-3-C^{13} exhibited certain pronounced differences from that of 2,4-dimethyl-3-pentanone. The data suggested that a study based on the infrared spectral frequencies of C^{13} labeled compounds, and some related deuterium and O^{18} derivatives, might be profitable in elucidating both the assigning of infrared frequencies and the degree to which various vibrations are coupled with others. Such information could help clarify certain regions of the spectrum, especially the 800–1500 cm.$^{-1}$ region where a great deal of controversy exists in the literature. As far as the degree to which various vibrations (in complex organic molecules) are coupled with others is concerned, a fairly good estimate could often be obtained from cases where the same molecule is isotopically labeled with either C^{13}, or O^{18}, or deuterium, in its various atoms. That such an estimate might not be too far off from values calculated by more rigorous methods is shown by the data regarding the carbonyl frequency of diisopropylketones.

RESULTS

This paper reports the results obtained from the investigation of the following diisopropylketones: 2,4-dimethyl-3-pentanone, 2,4-dimethyl-3-pentanone-3-C^{13}, 2,4-dimethyl-3-pentanone-O^{18}, 2,4-dimethyl-3-pentanone-2,4-d_2 and 2,4-dimethyl-3-pentanone-2,4-d_2-3-C^{13}. In addition, the carbonyl frequency of 2,2-dimethylpropionic-1-C^{13} acid is recorded. The infrared spectra were taken with a Perkin-Elmer double-beam Recording Infrared Spectrophotometer, Model 21. All frequencies reported in this paper were calculated from spectra taken in 4% and 12% (v./v.) solutions in carbon disulfide, except for those of the dimethylpropionic acids which were determined in 4% (v./v.) solutions in carbon tetrachloride. The purity of the samples used for the spectra was ascertained by vapor phase chromatography, a RECO Distillograph, Model D-2000, equipped with a 40% (w./w.) silicone oil on Celite column, being employed for that purpose. The composition of the

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[2] A. H. Nielsen, *Phys. Rev.*, **53**, 983 (1938).

[3] A. H. Nielsen and R. T. Lagemann, *J. Chem. Phys.*, **22**, 36 (1954).

[4] G. Glockler and M. M. Renfrew, *J. Chem. Phys.*, **6**, 340 (1938).

[5] H. C. Cheng, C. F. Hsueh, and Ta-You Wu, *J. Chem. Phys.*, **6**, 8 (1938).

C^{13} labeled ketones consisted of about 62% labeled and 38% unlabeled, according to the isotopic purity of the carbon dioxide used in their synthesis. The composition of the O^{18} labeled ketone consisted of about 35% labeled and 65% unlabeled, according to the isotopic purity of O^{18} water.

The pertinent spectral frequencies, the experimental frequency differences ($\Delta\nu$), and certain calculated $\Delta\nu$ values of the investigated compounds are presented in Tables I–III. The infrared spectra of some of them are shown in Figs. 1–3.

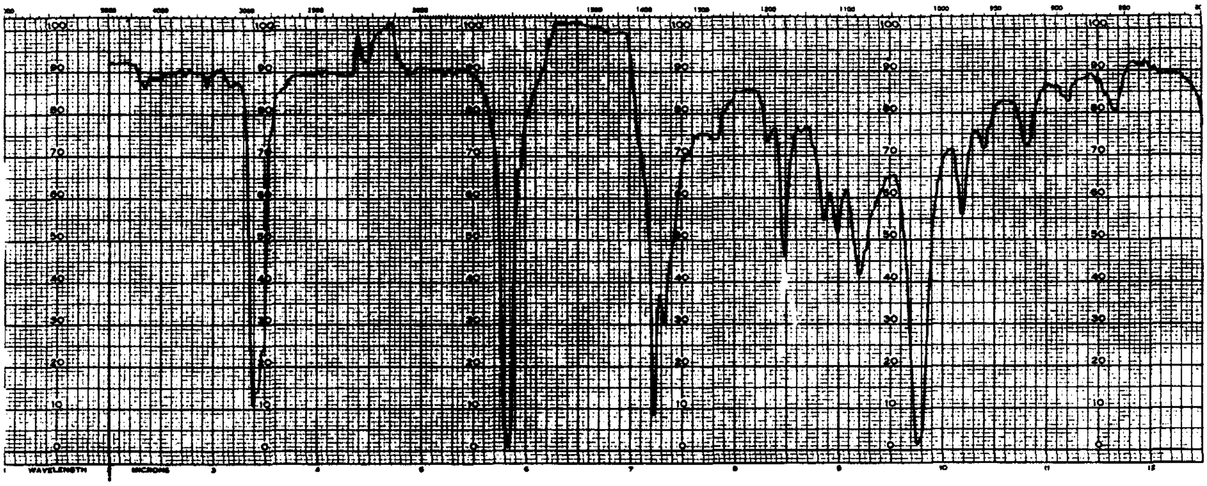

Fig. 1

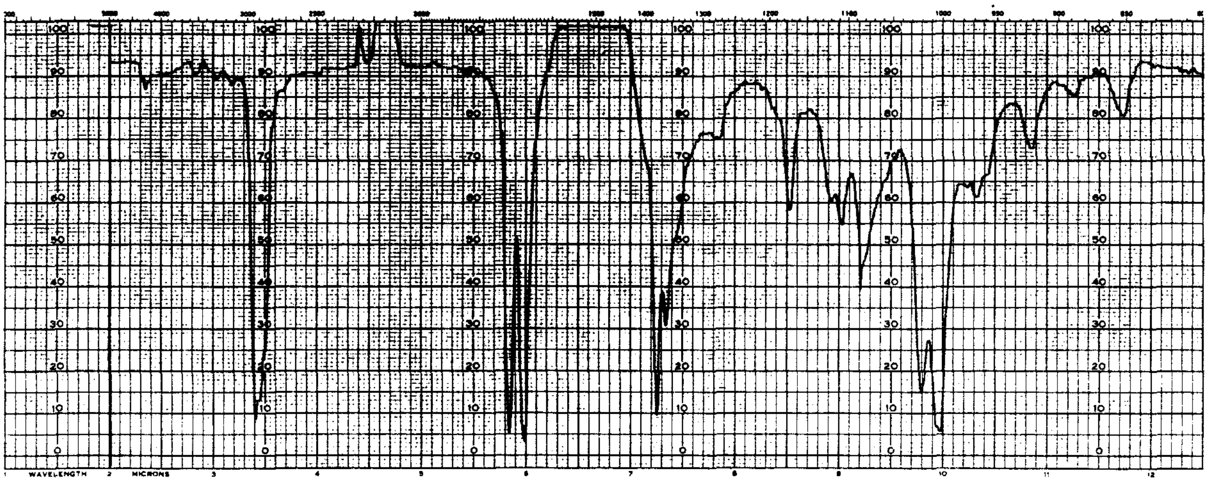

Fig. 2

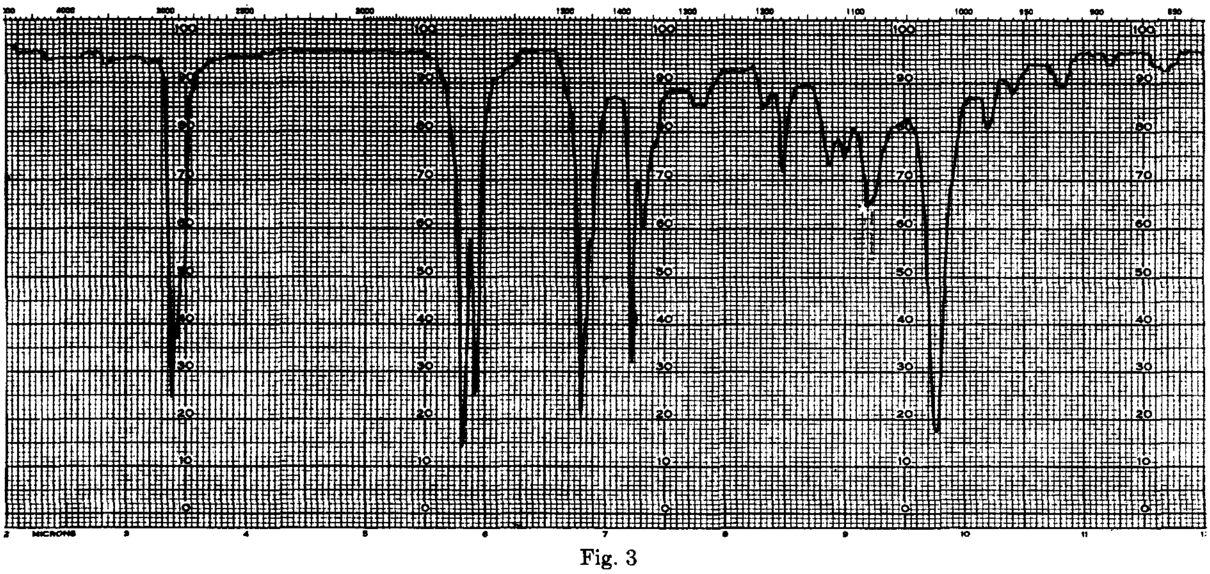

Fig. 3

TABLE I

INFRARED SPECTRAL FREQUENCIES OF DIISOPROPYLKETONES

Compound	Wave Number (cm.$^{-1}$)						$(\mu_2/\mu_1)^{1/2}$[a]
2,4-Dimethyl-3-pentanone	1712	1203	1129	1024	983	858	
2,4-Dimethyl-3-pentanone-3-C^{13}	1675	1190	1120	1004	972	853	
$\Delta\nu$ Experimental	37	13	9	20	11	5	
$\Delta\nu$ Calc. from (μC=O) and (μC^{13}=O)	38	27	25	23	22	19	1.0227
$\Delta\nu$ Calc. from (μC—C) and (μC^{13}—C)	34	24	22	20	19	17	1.020
$\Delta\nu$ Calc. from (μCO—$CH(CH_3)_2$) and ($\mu C^{13}O$—$CH(CH_3)_2$)	19	13	12	11	11	9	1.011

[a] μ_1 is the reduced mass calculated from the C^{12} compound and μ_2 the reduced mass calculated from the C^{13} compound.

TABLE II

INFRARED SPECTRAL FREQUENCIES OF 2,4-DIMETHYL-3-PENTANONE-O^{18}

Compound	Wave Number (cm.$^{-1}$)						$(\mu_2/\mu_1)^{1/2}$[a]
2,4-Dimethyl-3-pentanone	1712	1129	1203	1024	983	858	
2,4-Dimethyl-3-pentanone-O^{18}	1681	1129	1192	1024	983	858	
$\Delta\nu$ Experimental	31	0	11	0	0	0	
$\Delta\nu$ Calc. from (μC=O) and (μC=O^{18})	42		29				1.025

[a] μ_1 is the reduced mass calculated from the unlabeled ketone and μ_2 is the reduced mass calculated from the O^{18} labeled ketone.

TABLE III

INFRARED SPECTRAL FREQUENCIES OF 2,4-DIMETHYL-3-PENTANONE-2,4-d_2 AND 2,4-DIMETHYL-3-PENTANONE-2,4-d_2-3-C^{13}

Compound	Wave Number (cm.$^{-1}$)							
2,4-Dimethyl-3-pentanone-2,4-d_2	2175	2140	1712	1203	1052	1024	867	838
2,4-Dimethyl-3-pentanone-2,4-d_2-3-C^{13}	2175	2140	1675	1190	1042	1004	860	835
$\Delta\nu$ Experimental	0	0	37	13	10	20	7	3
$\Delta\nu$ Calc. from (μC=O) and (μC^{13}=O)			38	27	23	23	19	19
$\Delta\nu$ Calc. from (μC—C) and (μC^{13}—C)			34	24	20	20	17	17
$\Delta\nu$ Calc. from (μCO—$CD(CH_3)_2$) and ($\mu C^{13}O$—$CD(CH_3)_2$)			19	13	11	11	9	9

DISCUSSION

The most striking differences in the spectra of 2,4-dimethyl-3-pentanone and 2,4-dimethyl-3-pentanone-3-C^{13}, Fig. 1 and Fig. 2, respectively, occur in the carbonyl and the 1024 cm.$^{-1}$ regions.[6] The 1712 cm.$^{-1}$ frequency (the well known carbonyl stretch) is lowered to 1675 cm.$^{-1}$ upon C^{13} substitution in the carbonyl group of diisopropylketone. The shift, 37 cm.$^{-1}$, is in good agreement with the 38 cm.$^{-1}$ frequency difference calculated from the reduced masses of the carbonyl groups without taking into account the mass of the rest of the molecule. The same shift, 37 cm.$^{-1}$, is observed in the spectra of 2-methylpropionic-1-C^{13} and 2,2-dimethylpropionic - 1 - C^{13} acids, *e.g.*, 1701 cm.$^{-1}$ and 1664 cm.$^{-1}$ for 2,2-dimethylpropionic and 2,2-dimethylpropionic-1-C^{13} acids respectively.

The good agreement between experimental shift and the one obtained from theoretical calculations does not necessarily indicate that the carbonyl frequency of diisopropylketone is a diatomic vibration[7] without any contribution from other vibrations. One could very well explain it by suggesting that it is composed of 75% C=O stretch and 25% C—C stretch. It is interesting to note that the carbonyl shifts obtained by Braude and Turner[8] on the O^{18} carbonyl labeled 1-phenylallyl-*p*-nitrobenzoate and by Halmann and Pinchas[9] on the O^{18} labeled benzophenone correspond only to 75% of the theoretical shift. Francis[10] suggests, from a normal coordinate treatment of the skeletal modes of the acetone molecule, that the 1720 cm.$^{-1}$ frequency of acetone includes about 80% of C=O stretching and about 20% of C—C stretching vibra-

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[6] It might be interesting to report here the NMR spectrum of 2,4-dimethyl-3-pentanone-3-C^{13}. The coupling constant between the C^{13} and the methyl hydrogens (about 6 c.p.s.) is about twice as large as the coupling constant between the C^{13} and the tertiary hydrogens. The same coupling constants are observed with 2,4-dimethyl-3-pentanol-3-C^{13} and 2,4-dimethylpentane-3-C^{13}. Anomalies of this kind, involving either hydrogen-fluorine or hydrogen-mercury couplings, have been reported in the literature: M. Sharts and J. D. Roberts, *J. Am. Chem. Soc.*, **79**, 1008 (1957); H. H. Jaffe *et al.*, *J. Chem. Phys.*, **30**, 1422 (1959); P. T. Narasimhan and M. T. Rogers, *J. Am. Chem. Soc.*, **82**, 34 (1960).

[7] The term "diatomic vibration" is meant to indicate that the vibration is solely due to the motions of the two atoms involved, the rest of the atoms being treated as rigid.

[8] E. A. Braude and D. W. Turner, *Chem. & Ind.*, (*London*), 1223 (1955).

[9] M. Halmann and S. Pinchas, *J. Chem. Soc.*, 1703 (1958).

[10] S. A. Francis, *J. Chem. Phys.*, **19**, 942 (1951).

tions. Jones[11] has observed small carbonyl shifts, in the order of 1–5 cm.$^{-1}$, in some α-deuterated ketones in the steroid series, which again suggests that the carbonyl stretch in that series is not an uncoupled one. Halford's[12] treatment of the carbonyl force constant for unconjugated ketones clearly suggests that both the C=O and C—C stretchings are involved in the carbonyl frequency. In order to elucidate this point the infrared spectrum of 2,4-dimethyl-3-pentanone-O^{18} was examined. The carbonyl stretch was shifted by 31 cm.$^{-1}$, which corresponds to 74% of the calculated value. This finding is taken as an indication that the carbonyl frequency of diisopropylketone is a mixed one, composed of about 74% C=O stretch and 26% C—C stretch. The lack of evidence that any other vibrations are involved strongly supports Halford's treatment of the carbonyl force constant for unconjugated ketones.

The 1024 cm.$^{-1}$ frequency, a sharp strong band characteristic of many ketones, is shifted to 1004 cm.$^{-1}$ upon C^{13} carbonyl labeling, and is assigned here to an uncoupled C—C—C stretching between the carbon of the carbonyl group and the secondary carbons of the isopropyl groups. The experimental $\Delta\nu$ value, 20 cm.$^{-1}$, is in excellent agreement with the 20 cm.$^{-1}$ value calculated from the reduced masses of (C—C) and (C^{13}—C). The possibility that a C=O vibration might contribute is discounted by virtue of the data obtained from 2,4-dimethyl-3-pentanone-O^{18}, which show that the 1024 cm.$^{-1}$ frequency is unaffected. Likewise, the data of the dideuterated ketones reduce the contribution of any other vibration to insignificantly small proportions. The data, therefore, clearly point to the existence of an uncoupled vibration between three atoms which are deeply imbedded into the skeleton of a molecule. This, to the knowledge of this author, is the first case of this kind known.

The 1200 cm.$^{-1}$ frequency of ketones has been assigned by Kohlrausch[13] to the nonsymmetric C—C stretching vibration and by Francis[10] to the coupled vibrations[14] of C=O and C—C. Although the C^{13} data alone do not clearly differentiate between the two possibilities, when taken together with the results of 2,4-dimethyl-3-pentanone-O^{18} they support Francis' assignment. The 1129 cm.$^{-1}$, 983 cm.$^{-1}$, and 858 cm.$^{-1}$ frequencies are assigned to skeletal vibrations, all of which possess a considerable contribution of C—H vibrations, since they are all shifted to 1052 cm.$^{-1}$, 867 cm.$^{-1}$, and 838 cm.$^{-1}$ respectively upon dideuteration. The fact that these frequencies are unaffected in the spectrum of 2,4-dimethyl-3-pentanone-O^{13} excludes any C=O contribution.

EXPERIMENTAL

2,4-Dimethyl-3-pentanone-3-C^{13}. Preparation of 2,4-dimethyl-3-pentanone-3-C^{13} will be described elsewhere.

2,4-Dimethyl-3-pentanone-O^{18}. 2,4-Dimethyl-3-pentanone (0.3 ml.) was shaken for 18 hr. with 41% atom excess O^{18} water (0.5 ml.) in the presence of a small drop of 70% perchloric acid. The organic layer was separated and vapor phase chromatographed.

2,4-Dimethyl-3-pentanone-2,4-D_2. A solution of 2,4-dimethyl-3-pentanone (0.2 g.) in anhydrous ether (5 ml.) was shaken for 16 hr. with heavy water (5 g.) and sodium hydroxide (0.02 g.). The ether layer was separated, dried over anhydrous sodium sulfate, the ether evaporated, and the residue vapor phase chromatographed. The same procedure was followed in the preparation of 2,4-dimethyl-3-pentanone-2,4-d_2-3-C^{13}.

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(11) R. N. Jones, A. R. H. Cole, and B. Nolin *J. Am. Chem. Soc.*, **74**, 5662 (1952).

(12) J. O. Halford, *J. Chem. Phys.*, **24**, 830 (1956).

(13) K. W. F. Kohlrausch, *Ramanspektren* (Akademische Verlagsgesellschaft Becker and Erler, Leipzig, 1943), p. 103.

(14) It seemed surprising that certain frequency shifts, especially those of 1203 cm.$^{-1}$ and 983 cm.$^{-1}$ frequencies, could be well correlated with calculations based upon the reduced masses of the carbonyl and isopropyl groups (corresponding to the assumption that the isopropyl group vibrates against the effective mass of the carbonyl group). However, the data (Table III) of the 2,4-dideuterated ketones suggest that such a correlation is more fortuitous than significant. The 1203 cm.$^{-1}$ frequency is unaffected by deuteration, while a shift of about 4 cm.$^{-1}$ is expected from theoretical calculations; the shifts of the 1129 cm.$^{-1}$, 983 cm.$^{-1}$, and 858 cm.$^{-1}$ frequencies are too large to substantiate such a hypothesis.