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The Spectrum of Deuteroacetone in the Vacuum Ultraviolet

A Comparison with the Spectrum of Acetone

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The spectrum of acetone- d_6 of over 90 percent purity has been photographed in the region 2000–1300Å, with a dispersion of 4.14Å per mm. Data for the transition at about $51,000\text{ cm}^{-1}$ are presented together with new data on acetone in the same region. A discussion of the normal state of the acetones is given, and an analysis is made of the electronic spectra. It is shown that no vibrational frequency near 1200 cm^{-1} appears in the excited state of acetone- d_6 and that this frequency in acetone cannot be ascribed to the C–O vibration.

THE spectrum of acetone¹ and other simple ketones² consists of relatively sharp bands in the region $51,000\text{--}54,000\text{ cm}^{-1}$. In all attempted analyses of these spectra there has been found a frequency in the neighborhood of 1200 cm^{-1} which has been ascribed to the C–O vibration. It is well known that this frequency has a value of about 1700 cm^{-1} in the normal states of compounds which contain this group. The electronic spectrum of deuterioformaldehyde³ in the region $30,000\text{ cm}^{-1}$ has revealed also the presence of the 1200-cm^{-1} frequency which must be interpreted as the carbonyl frequency in this case.

We have prepared samples of almost pure acetone- d_6 . Over 90 percent of the hydrogen has been replaced by deuterium as shown by analysis and by the relative simplicity of the spectrum. The spectrum of these samples has been examined in the $50,000\text{-cm}^{-1}$ region in an attempt to find this 1200-cm^{-1} carbonyl frequency. Such a frequency is shown definitely to be absent. The interpretation of such a frequency in acetone (and presumably in other ketones in this region) as the C–O frequency therefore becomes untenable, since the electronic transitions are surely the same. In the subsequent discussion an alternate interpretation will be given.

EXPERIMENTAL

The deuteroacetone was prepared by repeated exchange of acetone (Merck reagent, aldehyde free) with 99.6 percent D_2O using NaOD as catalyst.⁴ After separation from most of the water by distillation in a vacuum through anhydrous calcium chloride, it was dried with anhydrous CuSO_4 and purified by vacuum distillation. A small sample was burned to water and analyzed for D content by the thermal conductivity method.⁵ A sample showing over 90 percent D content could be produced after four exchanges.

The plates were taken with a normal incidence vacuum spectrograph² containing a 2-meter radius 120,000-line grating. The light source was a conventional hydrogen discharge operated at 3–4 kilowatts. Exposure times were 20 minutes with Eastman 103a-0 ultraviolet sensitized plates. The deuteroacetone vapor was introduced through calibrated volumes directly into the spectrograph which was shut off from the pumps during exposures. It was estimated that the pressures of deuteroacetone in the spectrograph were from 0.005 to 0.07 mm on the assumption that the vapor pressures of acetone and deuteroacetone are the same at 0°C . Most plates of acetone were taken in a pressure range of 0.005 to 0.04 mm. A few plates of acetone were taken at high pressures (5–20 mm) in the spectrograph to give the lowest frequency bands. Since we did

* Part of a dissertation presented to the Faculty of the Graduate School of the University of Rochester in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

¹ W. Albert Noyes, Jr., A. B. F. Duncan, and Winston M. Manning, *J. Chem. Phys.* **2**, 717 (1934).

² A. B. F. Duncan, *J. Chem. Phys.* **8**, 444 (1940).

³ E. H. Ebers, Ph.D. Thesis (Harvard University, 1935).

⁴ (a) O. Reitz, *Zeits. f. physik. Chemie* **A179**, 119 (1937).
(b) W. D. Walters and K. F. Bonhoeffer, *Zeits. f. physik. Chemie* **A182**, 265 (1938).

⁵ P. Harteck, *Zeits. f. Electrochemie* **44**, 3 (1938).

not have enough deuterioacetone to fill the spectrograph (volume about 225 liters) at such high pressures, a quartz cell 20 cm long was introduced between the source and the slit and correspondingly higher pressures (up to 70 mm) of deuterioacetone used to bring out the low frequency bands. The absorbing column was at room temperature.

Most of the plates were measured with a precision comparator using the following reference lines:⁶

C I 1930.930,
N I 1745.250,
N I 1742.734.

The error in measurement of sharp bands in this way probably does not exceed 2–3 cm⁻¹. The dispersion was about 4.14 Å per mm.

The bands appearing only at very high pressures could not be measured in this way because these standard lines were absorbed, and no additional standard lines were present in this region. Recourse had to be made to a rather crude method of measurement from enlarged reproductions of these spectra, utilizing standard lines in adjacent spectra. The error in these measurements is therefore higher but still less than 7 cm⁻¹ as judged from measurements of many different plates.

The experimental results of the electronic spectra are given in Table II, but before discussion of this table the normal state of acetone and deuterioacetone will be considered.

NORMAL STATE

Analysis of the spectra of acetone and deuterioacetone must start with a discussion of the symmetry properties of the molecules and their normal vibrations. A general treatment requires no symmetry (*C*₁), although *C*_{2v} symmetry is possible for a rigid and symmetrical arrangement of the methyl groups relative to one plane through the C–O group.

However, if we treat the methyl groups as points, or assume that the groups rotate freely, the model certainly corresponds to symmetry *C*_{2v} and the discussion appears to be profitable. This may be justified if the force constants which

⁶ J. C. Boyce and J. T. Moore, *Provisional Wavelength Identification Tables for the Vacuum Ultraviolet* (1941).

TABLE I. Forms of vibration and Raman frequencies of acetone and deuterioacetone.

Form of vibration (after Wu) ^a							
Notations							
Present Engler, ^b	ω_3	ω_1	ω_2	ω_4	ω_5	ω_6	ω_H
Kohlrausch and Pongratz ^c	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6	ω_2'
Aston and Schumann ^d	$\nu_2(\pi)$	$\nu_1(\pi)$	$\delta(\pi)$	$\nu_1(\sigma)$	$\delta_1(\sigma)$	$\delta_2(\sigma)$	$2\delta(\pi)$
Symmetry	<i>A</i> ₁	<i>A</i> ₁	<i>A</i> ₁	<i>B</i> ₁	<i>B</i> ₁	<i>B</i> ₂	<i>A</i> ₁
Present assignment of acetone frequencies from data of reference e	1710	1066	787	530	488	391	1356
Present assignment of acetone- <i>d</i> ₆ frequencies from Engler's data	1710	895	700	483	413	335	1093
Depolarization ratios (acetone)							
Reference e	0.38	0.64	0.20	0.70	0.90	0.87	0.60
Edsall and Wilson ^f	<i>P</i>	<i>P</i>	<i>P</i>	<i>D</i>	<i>D</i>	<i>D</i>	<i>P</i>
Other assignments of acetone frequencies							
Kohlrausch and Pongratz	1710	787	530	1066	391*	391*	1356
Engler	1710	787	530	1066	391	—	1356
Aston and Schumann	1710	787	391	1066	530	530	1220
Acetone- <i>d</i> ₆ frequencies							
Engler's assignment	1710	700	483	1038	335	—	1038
Teller product (calc.)		1.27		1.16		1.02	
(obs.)		1.34		1.31		1.17	

^a T. Y. Wu, *Vibrational Spectra and Structure of Polyatomic Molecules* (Prentice-Hall, Inc., New York, 1940), p. 208.

^b See reference 7.

^c See reference 10.

^d See reference 13.

^e See reference 8.

^f See reference 11.

* Kohlrausch and Pongratz were uncertain whether to assign 391 to ω_5 or ω_6 .

determine the internal hydrogen frequencies do not affect appreciably the vibrations of the Me₂CO framework. There will be six frequencies belonging to this four-atom model which have symmetries *A*₁ (3), *B*₁ (2), *B*₂ (1). All six frequencies are permitted in the Raman effect and in the infra-red spectra. In the Raman effect the three frequencies of representation *A*₁ should have low depolarization ratios and the other three should have depolarization ratios of $\frac{3}{4}$ for light initially unpolarized.

The Raman spectrum of deuterioacetone was investigated by Engler,⁷ but depolarization

⁷ W. Engler, *Zeits. f. physik. Chemie* **B35**, 433 (1937).

ratios were not obtained. The Raman spectrum of acetone has been obtained by many workers⁸ and depolarization data are available. The infra-red spectrum of acetone vapor has been studied.⁹ Previous attempts at analysis have been made, and their conclusions relative to the Me_2CO frequencies for acetone and deuterioacetone together with the present assignment are shown in Table I. It should be pointed out that the wide divergencies in assignment are due either to ignorance of the data on depolarization of Raman lines or in interpretation of the depolarization data themselves. For example, the 1066-cm^{-1} line was considered depolarized by Kohlrausch and Pongratz¹⁰ and by Engler. More recent work of Edsall and Wilson¹¹ (especially their Fig. 4) shows that it must be polarized, which agrees with the earlier work of Simons.¹² The 530-cm^{-1} line has a depolarization ratio of 0.70, and this has been interpreted as indicating that the line is polarized by Kohlrausch and Pongratz and by Engler; but Edsall and Wilson show that this line is depolarized. Kohlrausch and Pongratz inconclusively assign 391 cm^{-1} to ω_5 or ω_6 , and Engler assigns this to ω_5 .

Our present assignment is based on the following reasoning. The depolarization data show rather unambiguously that the A_1 frequencies are 1710, 1066, and 787, and the B frequencies are 530, 488, and 391.¹³ The vibration ω_6 of symmetry B_2 should have the lowest frequency so it is assigned the value 391. The 1710-cm^{-1} vibration of A_1 may be assigned to the model unambiguously. 1066 and 787 of A_1 and 530 and 488 of B_1 are assigned arbitrarily to stretching and bending, respectively, because stretching fre-

quencies usually appear to be larger. This is, however, of no importance to our discussion.

Our assignments of the deuterioacetone lines differ from Engler for the following reasons. Our reassignment of 530 and 488 to B_1 in acetone will automatically change Engler's assignments to agree with ours in this respect since he has correlated 483 and 413 in deuterioacetone with the above acetone values. Our choice of the correspondence of 1066 with 895 in acetone and deuterioacetone rather than the correspondence of 1066 with 1038 proposed by Engler arises from this consideration. In the electronic spectra, to be discussed later, very few bands arising from vibrational levels of the ground state are found. In acetone these show frequency differences of 1066 and 1357 in acetone, and 895 and 1087 in deuterioacetone. From similarity of appearance, pressure dependence at constant temperature, and temperature dependence, 1066 definitely corresponds to 895 and 1357 to 1087, in acetone and deuterioacetone, respectively. The frequencies 1357 and 1087 in the two molecules are assigned to symmetrical hydrogen bending and designated as ω_H in Table I. The other symmetrical hydrogen frequency (stretching) is not necessary to our discussion.

Some confirmation of the above assignments may be found in the calculated and observed values of the Teller (or Redlich) isotope product ratios¹⁴ shown in Table I. On the simple assumption that the force constants are unchanged, poor agreement with experiment was obtained. This is to be expected since in the C_{2v} model we are substituting CH_3 by CD_3 and not H by D. To refine these calculations, we may make assumptions regarding the change of force constants with distance in the two molecules since the CH_3 and CD_3 groups are considered as units. It may be assumed that the masses of CH_3 and CD_3 act at their respective centers of gravity and the C-H and C-D distances are not changed. In this case the C-C distance must be different in the two molecules; or if the C-C distance is to remain fixed, different effective masses for CH_3 and CD_3 must be used giving the

⁸ F. F. Cleveland, M. J. Murray, J. R. Coley, and V. I. Komarewsky, *J. Chem. Phys.* **10**, 18 (1942).

⁹ (a) Donna Price, *J. Chem. Phys.* **9**, 725 (1941). (b) W. W. Coblenz, *Investigations of Infra-Red Spectra. Part I* (Carnegie Institution Publication, 1905).

¹⁰ K. W. F. Kohlrausch and A. Pongratz, *Zeits. f. physik. Chemie* **B27**, 180 (1934).

¹¹ J. T. Edsall and E. B. Wilson, *J. Chem. Phys.* **6**, 124 (1938).

¹² L. Simons, *Soc. Sci. Fenn. Com. Phys. Math.* **6**, No. 13 (1932).

¹³ There are two low frequency lines 587 and 731 cm^{-1} of very low intensity and unknown depolarization which do not fall into any assignment. Lines corresponding to these do not appear in the Raman spectrum of deuterioacetone. The acetone frequency 901 cm^{-1} appears strongly in the infra-red (880 cm^{-1}) and may be associated with internal rotation [cf. S. C. Schumann and J. G. Aston, *J. Chem. Phys.* **6**, 485 (1938).]

¹⁴ (a) W. R. Angus, C. R. Bailey, J. B. Hale, C. K. Ingold, A. H. Leckie, C. G. Raisin, J. W. Thompson, and C. L. Wilson, *J. Chem. Soc.*, p. 971 (1936). (b) O. Redlich, *Zeits. f. physik. Chemie* **B28**, 371 (1935).

TABLE II. Wave numbers of bands in acetone and acetone- d_6 .

Transitions $\nu = \nu_0 + \omega_s'$										
Acetone										
51181	ω_6' (269)	51450	ω_5' (315)	51496	ω_2' (714)	51895	ω_1' (1047)	52228	ω_H' (1194)	52375
51199	(276)	51475	(327)	51526	(715)	51914	(1049)	52248	(1194)	52393
51227			(328)	51555	(716)	51943			(1192)	52419
51241										
51253			(326)	51579	(714)	51967	(1042)	52295	(1190)	52443
51287					(723)	52010	(1036)	52323	(1190)	52477
51313					(742)	52055	(1038)	52351	(1200)	52513
51350					(724)	52074			(1186)	52536
Acetone- d_6										
51302	ω_6' (237)	51539	ω_5' (259)	51561	ω_2' (612)	51914	ω_1' (816)	52118	ω_H' (906)	52208
51317			(266)	51583	(615)	51932	(821)	52138	(906)	52223
51333			(273)	51606	(614)	51947	(816)	52149	(908)	52241
								52162		
51354			(273)	51627	(615)	51969	(819)	52173	(907)	52261
51374					(610)	51984	(820)	52194	(912)	52286
51390					(614)	52004			(910)	52300
51421									(913)	52334
51460									(912)	52372
51511										
Transitions $\nu = \nu_0 + 2\omega_1'$					Transitions $\nu = \nu_0 + \omega_H' + \omega_1'$					
Acetone										
ω_1'	ω_1'							ω_H'	ω_1'	
(1047+1041)		53269						(1194+1041)		53416
(1049+1042)		53290						(1194+1041)		53434
(1042+1041)		53336						(1190+1027)		53470
(1036+1044)		53367						(1190+1026)		53503
								(1186+1021)		53557
Acetone- d_6										
ω_1'	ω_1'							ω_H'	ω_1'	
(816+819)		52937						(906+815)		53029
(821+814)		52952						(906+817)		53040
(816+819)		52968						(908+814)		53055
(819+814)		52987						(910+806)		53106
								(912+792)		53164
Transitions $\nu = \nu_0 - \omega_1''$					Transitions $\nu = \nu_0 + \omega_s' - \omega_s''$					
Acetone										
ω_1''	ω_H''							ω_5'	ω_5''	
(1062)	(1352)	50119		49829				(315-487)		51009
(1063)	(1357)	50136		49842				(327-503)		51023
(1064)	(1356)	50163		49873				(328-500)		51055
(1070)	(1358)	50183		49895				(326-503)		51076
(1070)		50217								
Acetone- d_6										
ω_1''	ω_H''							ω_5'	ω_5''	
(883)	(1085)	50419		50217				(259-404)		51158
(884)	(1087)	50433		50230				(266-408)		51175
(881)	(1089)	50452		50244				(273-410)		51196
(883)	(1083)	50471		50271				(273-414)		51213
										51234

same result. We have assumed that only one (stretching) constant changes, which affects only the products for A_1 and B_1 . The value for A_1 is brought into what is probably satisfactory agreement. The change of the constant with distance was calculated from the rules of Badger¹⁵

and Clark¹⁶ which gave identical results. The residual lack of agreement in the isotope product ratios is ascribed to neglect of the numerous

¹⁵ R. M. Badger, J. Chem. Phys. 2, 128 (1934).

¹⁶ C. H. Douglas-Clark, Trans. Faraday Soc. 31, 1017 (1935).

possible interaction constants¹⁷ in the potential energy, whose magnitudes must mostly be guessed. These are constants not only pertinent to the model C_{2v} being discussed but also those for interaction between motions of the methyl groups with the rest of the molecule.¹⁸ These interaction constants should affect particularly the B_1 and B_2 ratios. It may be pointed out, however, that any change in our assignment of B_1 and B_2 frequencies makes the products generally worse.

ELECTRONIC TRANSITION

Table II shows measurement of acetone and deuterioacetone in the region 40,000–60,000 cm^{-1} from recent plates. Figure 1 shows key transitions in an energy level diagram. Figure 2 shows a few microphotometer traces from representative plates. The data are arranged in Table II so that with these figures the analysis and discussion will be clear. To avoid confusion the frequencies of acetone bands only are used in the following discussion. Corresponding deuterioacetone bands may be easily found from Table II.

The positions of all bands are expressed by an equation $\nu = \nu_0 + \sum n\omega_i' - \omega_i''$ where ν is the frequency in cm^{-1} of the transition, ν_0 the frequency of the electronic transition between non-vibrating

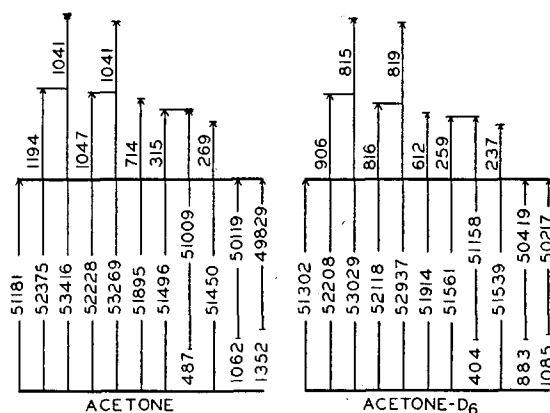


FIG. 1. Key transitions in acetone and acetone- d_6 .

states, ω_i'' and ω_i' are vibration frequencies of the normal and excited states of the molecule,

¹⁷ B. L. Crawford, Jr., and S. R. Brinkley, Jr., J. Chem. Phys. **9**, 69 (1941).

¹⁸ O. Redlich and L. E. Neilson, J. Am. Chem. Soc. **65**, 654 (1943).

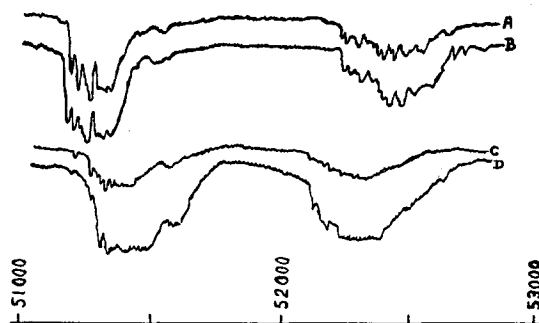


FIG. 2. Microphotometer traces of typical plates. A, acetone, 0.005-mm pressure. B, acetone, 0.01-mm pressure. C, acetone- d_6 , 0.01-mm pressure. D, acetone- d_6 , 0.02-mm pressure.

respectively, and n the number of quanta of vibration ω_i' excited. Most transitions are seen to be of the simple type $\nu = \nu_0 + \omega_i'$ where one quantum of vibration is added to the electronic transition. There are a few cases in which more than one quantum of vibration is added but no long progressions. The notation used in regard to i in ω_i may appear arbitrary, but we followed the conventions of others where any consistency exists. In any case, the notation will be apparent from Table I.

Most of the bands consist of numerous groups of sub-bands, possibly due to the unresolved rotational structure. The total width of the bands is quite consistent with reasonable values of the moment of inertia. For example, ν_0 itself consists of 6 and possibly 8 sub-bands, of which 51, 181, 51,199, and 51,253 appear to be most important. In Fig. 1 this appears as a single transition 51,181. Other transitions $\nu_0 + \omega_i$, etc., also consist of such sub-bands which show striking similarities both in visual examination of plates and differences from the ν_0 sub-bands. Corresponding sub-bands appear in the same row in the table. The values of ω_i are given in parentheses for corresponding sub-bands. The absolute values of ω_i' obtained in this way are probably not too significant. Since we have not attempted to interpret the sub-bands and there appears little hope of doing this, we have rather arbitrarily chosen to take differences from sub-bands which appeared to be similar.

Since all measurements are made from ν_0 (51,181 cm^{-1}), the choice of this as the origin of the electronic transition may be questioned. This

band has the highest intensity of the whole transition. (Actually a sub-band 51,253 of ν_0 is more intense, but this does not affect our frequency differences since the corresponding sub-band is always most intense in other bands.) No other bands appear to the red until the temperature or pressure is greatly increased, and when this is done, the only bands appearing are separated from ν_0 by normal state frequencies. These facts all point to an allowed electronic transition with the above origin. If a forbidden electronic transition were present instead, it would be allowed by a vibration B_1 or B_2 excited in either the normal or excited state. The existence of two high temperature bands separated from our chosen ν_0 by exact normal state frequencies gives the most positive evidence against 51,181 cm^{-1} being a transition $\nu_0 + \omega_B'$, where ω_B' is the vibration excited in the upper state which allows the forbidden transition. If this were so, then it would be necessary that the frequencies obtained from the high temperature bands must be diminished by ω_B' (of symmetry B_1 or B_2) and still give other normal state frequencies. This may be tested since we have the two observed frequencies. It follows that $\omega_H'' - \omega_1''$ must be the exact difference of two other normal state frequencies $\omega_x'' - \omega_y''$ and that $(\omega_H'' + \omega_1'') - (\omega_x'' + \omega_y'') = 2\omega_B'$. Now ω_B' must be less than ω_B'' . Substitution of all known values of ω_x'' and ω_y'' gives values of ω_B' greater than any known ω_B'' . It must be further pointed out that the experimental value of the intensity of the whole electronic transition¹⁹ determined in solution and the theoretical calculations²⁰ indicated that the transition is allowed. Exactly the same conclusion may be drawn in regard to the transition in deuterioacetone.

If ν_0 has been correctly assigned on the basis of these considerations, the interpretation of the other excited state frequencies requires little comment. The most obvious frequency difference in acetone is 1194. Even visual examination shows that this frequency is absent in deuterioacetone. Addition of this frequency to ν_0 (51,302) brings us to a region of relatively high transmission. We must conclude, therefore, that 1194

cm^{-1} in acetone cannot be assigned to the C—O frequency. The corresponding frequency of equal prominence which we do find in deuterioacetone is 906 cm^{-1} . It is concluded that 1194 cm^{-1} in acetone and 906 in deuterioacetone are due to hydrogen bending in the methyl groups which correspond to 1357 cm^{-1} and 1093 cm^{-1} of the normal states. It appears probable that the frequency of about 1200 cm^{-1} common to the excited states of ketones and aldehydes may be ascribed to hydrogen bending, except in the case of formaldehyde. In this case we cannot question its assignment to C—O stretching.

The correlation of the other normal and excited state frequencies which we have made will be apparent from Tables I and II. Of these the most prominent in the excited state is 1047, and it appears reasonable to assign it to a totally symmetrical vibration. It may be pointed out that this is the only frequency giving even a short progression. Of the remaining three excited state frequencies only 315 cm^{-1} requires additional comment, because of its connection with the transition $\nu = \nu_0 + \omega_5' - \omega_5''$ at 51,009 cm^{-1} . The correlation of these three frequencies does not differ materially from previous suggestions of Noyes, Duncan, and Manning.

The band at 51,009 cm^{-1} in acetone is separated from ν_0 by only 172 cm^{-1} . Since we have not found independent evidence of a frequency of this magnitude in either the upper or lower state, the transition may arise from an excited level in the ground state and end on an excited level in the upper state. It appeared reasonable that the same vibration was concerned in both states. The difference between 51,009 cm^{-1} and ν_0 should then be equal to a difference $\omega_i'' - \omega_i'$. The only known low normal frequency satisfying this condition is 488, which is 321 in the excited state. That the frequency must be a low one is shown from a qualitative study of the temperature dependence of the band. Support of this assignment is found in the spectrum of deuterioacetone where the corresponding band 51,158 cm^{-1} is separated from ν_0 by 144 cm^{-1} . This is approximately the difference $\omega_5'' - \omega_5'$ for deuterioacetone.

A comparison of the present results with those obtained earlier by Noyes, Duncan, and Manning

¹⁹ H. Ley and B. Arends, *Zeits. f. physik. Chemie* **B12**, 132 (1931).

²⁰ H. L. McMurray, *J. Chem. Phys.* **9**, 231 (1941).

in the same region apparently shows some inconsistencies which require comment at this point. The changes in numerical values of wave numbers of sub-bands are due partly to better resolution of the sub-bands and partly to changed values of reference lines. Disagreement with the former analysis is mainly in details concerning the sub-bands. A completely satisfactory analysis appears impossible without a quantitative interpretation of the sub-bands.

Our Table II, which we wished to represent the results of interpretation rather than a list of all transitions found, is incomplete in two respects. First, our data on deuterioacetone do not extend to frequencies as high as have been observed in acetone. Our data on acetone above $53,600\text{ cm}^{-1}$ are less complete than the former results of Noyes, Duncan, and Manning, though in no essential disagreement. We have accordingly omitted these from Table II. Second, we have omitted some transitions which appear at high pressures on the low frequency side of the main transitions in both acetones. We doubt

whether these actually belong to the transitions they appear to precede, but a list of the bands is given and in parentheses following, the transition to which they may belong. In acetone we have found: 51,113 and perhaps others (ν_0); 52,168, 52,187, ($\nu_0 + \omega_1'$); 62,114, 52,131 ($\nu_0 + \omega_2'$); 53,068, 53,137 ($\nu_0 + 2\omega_1'$); 53,390 ($\nu_0 + \omega_H' + \omega_1'$); 50,951 and others ($\nu_0 + \omega_5' - \omega_8''$). In acetone- d_6 we have found: 51,265, 51,284, and perhaps others (ν_0); 52,029, 52,062 ($\nu_0 + \omega_1'$); 52,881, 52,911 ($\nu_0 + 2\omega_1'$); 53,006 ($\nu_0 + \omega_H' + \omega_1'$).

Our results on the spectrum of deuterioacetone at frequencies higher than 53,200 are incomplete. We were unable to find other bands belonging to this transition. We do find, however, the analog of the next electronic transition in acetone. In acetone this is at 60,079 and in deuterioacetone at 60,071. It is remarkable that there is so little difference in ν_0 values. The strongest transition in deuterioacetone is estimated to occur at a slightly higher frequency than in acetone (where it is at $65,218\text{ cm}^{-1}$), but no measurement was made.