[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

Electronic and Vibrational States of Biacetyl and Biacetyl-d_6 I. Electronic States[1]

BY JEROME W. SIDMAN[2] AND DONALD S. MCCLURE

RECEIVED AUGUST 18, 1955

The absorption and emission spectra of biacetyl and biacetyl-d_6 have been studied at 20°K. and at 4°K. in the crystalline state from 15,000 to 40,000 cm.$^{-1}$ and in solid solution in 2-butanone. A weak transition has been observed in the visible region and is assigned to a singlet–triplet absorption transition. An effort is made to correlate this weak absorption with the intense green emission of biacetyl. The very weak blue fluorescence of biacetyl and the stronger absorption in the blue region are shown to correspond to the same electronic transition, which is allowed by symmetry. Absorption transitions between the ground state and three excited electronic states show vibrational structure, which has been analyzed. Emission transitions from two of these excited electronic states to the ground state also show vibrational fine structure. In addition, evidence is presented for the existence of other excited electronic states. Assignments are proposed for the excited states in terms of the LCAO–MO predictions for biacetyl.

I. Introduction

The compound 2,3-butanedione ($CH_3COCOCH_3$), commonly called biacetyl, has been the subject of considerable study. Part of the interest in this compound is due to the fact that it exhibits an intense green emission when excited by blue or purple light.[3] Biacetyl is one of the products in the photolysis of acetone,[4] and biacetyl itself undergoes photochemical reactions.[5] The electronic states of biacetyl have been discussed in terms of the LCAO–MO theory,[6] and the infrared spectra have also been measured and interpreted.[7] In spite of the large number of investigations, no detailed interpretation of the electronic–vibrational spectrum has been proposed, due to the fact that the spectra are very complex in the vapor at room temperature, and appear almost diffuse due to the overlapping of many vibrational–electronic transitions.

In this investigation, the absorption and emission spectra of biacetyl have been studied at 20 and 4°K., in the crystalline state and in a solid solution in 2-butanone. The absorption and emission spectra of the crystal at low temperatures show considerable sharp vibrational structure, and these spectra can be analyzed and interpreted in greater detail than is possible in the vapor.

II. Experimental

Eastman Kodak Co. white label biacetyl was distilled several times under reduced pressure and was stored in the dark over Dry Ice. The boiling point, refractive index and infrared spectra all indicated that the material was pure. The severest test of purity was the reproducibility of the absorption and emission spectra upon repeated fractionation of the biacetyl. Biacetyl-d_6 was prepared by acid-catalyzed exchange with 99.6% D_2O.[8] One exchange with 41% D_2O followed by two exchanges with 99.6% D_2O gave a sample containing 96% replacement of H by D, and the isotopic composition of this sample is 80% D_6, 16% D_5H, 1.5% D_4H_2.[9]

Biacetyl crystals were grown by freezing in liquid nitrogen a sample of biacetyl contained in a cell consisting of two quartz discs separated by a brass spacer of the appropriate thickness. The spectra were measured on a large Hilger spectrograph with a Littrow quartz prism, and preliminary measurements were made with a medium Hilger quartz spectrograph. The spectrograph was equipped with a Wollaston prism in order to study the absorption spectra of single crystals. The reciprocal linear dispersion of the large spectrograph was 6 Å./mm. at 4000 Å. and 12 Å./mm. at 5000 Å. The resolution was limited by the sharpness of the spectra under the conditions of the experiments. In biacetyl crystal at 20 or 4° K., the width of an absorption "line" is about 15 cm.$^{-1}$. The frequency of a line is therefore accurate to about 4 cm.$^{-1}$, and frequency differences are accurate to about 6 cm.$^{-1}$.

Spectra were recorded with the sample immersed in the liquid refrigerant. A tungsten lamp or a high pressure xenon arc was used as a light source for measuring absorption spectra. Emission spectra were obtained by exciting biacetyl with λ 4047 Å. and λ 3660 Å. from a high pressure mercury arc with the Corning filters 4308 and 5970 and a 2 cm. path of a saturated aqueous solution of $CuSO_4 \cdot 5H_2O$. This filter combination completely removed the intense λ 4358 Å. source line as well as the intense source lines in the green and orange. Spectra were recorded on Eastman Kodak Co. 103-O or F plates, using a 50 μ slit and recording iron arc calibration spectra without moving the plate holder. Exposure times ranged from two minutes for some of the absorption spectra to three hours for the very weak emission spectra. The wave lengths were determined from measurements under a comparator microscope by using a Hartmann dispersion formula, and wave lengths were converted to wave numbers (cm.$^{-1}$) *in vacuo*.

III. Results

A. Absorption Spectra of Crystalline Biacetyl.

1.—An electronic–vibrational transition begins at 22,873 cm.$^{-1}$ (22,896 cm.$^{-1}$ in Ac_2-d_6) and is seen in a 0.025 mm. crystal. A microphotometer trace of this transition is shown in Fig. 1, and the vibrational analyses are given in Tables I and II. This absorption transition has been studied by many previous workers. Lewis and Kasha[10] have studied the transition in the vapor, and Forster[11] has recently studied the solvent effects on this transition in solution. In so far as it can be compared, the transition in the crystal is similar to the transition in solution or in the vapor. The transition is shifted only a few hundred cm.$^{-1}$ in going from vapor to crystal, and the vibrational envelope is quite similar (Fig. 1). However, the transition is much sharper in the crystal than in the vapor.

---

(1) (a) This work was partially supported by the U. S. Office of Naval Research under Contract N6 ori-211-T.O.III. A preliminary report of the work was presented at the Division of Physical and Inorganic Chemistry, Paper 55, at the meeting of the American Chemical Society in New York City, September, 1954. (b) From the dissertation submitted by Jerome W. Sidman to the Graduate Faculty of the University of California, June, 1955, in partial fulfillment of the requirements for the Ph.D. degree.

(2) Du Pont Teaching Fellow, 1954–1955.

(3) G. M. Almy and P. R. Gillette, *J. Chem. Phys.*, **11**, 188 (1943).

(4) M. S. Matheson and J. W. Zabor, *ibid.*, **7**, 536 (1939).

(5) J. G. Roof and F. E. Blacet, THIS JOURNAL, **63**, 1126 (1941).

(6) H. M. McMurry, *J. Chem. Phys.*, **9**, 231, 241 (1941).

(7) T. Miyazawa, *J. Chem. Soc. Japan*, **74**, 743 (1953).

(8) (a) W. D. Walters, THIS JOURNAL, **63**, 2850 (1941); (b) H. C. Brown and C. Groot, *ibid.*, **64**, 2223 (1942).

(9) Dr. Amos S. Newton of the Radiation Laboratory kindly analyzed the deuterated biacetyl on the mass spectrometer.

(10) G. N. Lewis and M. Kasha, THIS JOURNAL, **67**, 994 (1945).

(11) L. S. Forster, *ibid.*, **77**, 1417 (1955).

TABLE I

VIBRATIONAL ANALYSIS OF STRONG VISIBLE ABSORPTION[a] OF Ac_2 CRYSTAL (Crystal 0.025 mm.)

Int.	ν, cm.$^{-1}$	ν − 22,873	Assignment	Assignment
w	22805	..		
w	22845	..		
vs	22873	0	$I^1A_u \leftarrow {}^1A_g$	
m	22908	35	35	
vs	22941	69	2(35)	
m	22975	102	3(35)	
s c	23011	138	4(35)	
m c	23047	174	5(35)	
m c	23066	193	193?	
m c	23105	232	193 + 35	
m c	23138	265	193 + 2(35)	
w	23171	298	193 + 3(35)	
w	23201	328	193 + 4(35)	
s	23229	356	356	
w	23264	391	356 + 35	
m	23298	425	356 + 2(35)	
w	23332	459	356 + 3(35)	
s	23368	495	495	
m	23403	530	495 + 35	
s	23436	563	495 + 2(35)	
m	23468	595	495 + 3(35)	
m	23501	628	495 + 4(35)	
m	23534	661	495 + 5(35)	
m	23562	689	495 + 6(35)	
w	23590	717	2(356)	
w	23621	748	2(356) + 35	
vw	23659	786	2(356) + 2(35)	
w	23682	809		
w	23763	890		
w	23801	928		
s	23871	998	998	
m	23904	1031	998 + 35	
s	23941	1068	998 + 2(35)	
w	23975	1102	998 + 3(35)	
vs	24009	1136	1136	
m	24044	1171	1136 + 35	
s	24080	1207	1136 + 2(35)	
m	24113	1240	1136 + 3(35)	
m	24145	1272	1136 + 4(35)	
w	24188	1315		
w	24204	1331		
m	24227	1354	998 + 356	
w	24257	1384	998 + 356 + 35	
w	24276	1403		
w	24297	1424	998 + 356 + 2(35)	
m	24320	1447	1447	
vw	24343	1470	1447 + 35	
m	24365	1492	998 + 495	1136 + 356
m	24401	1528	998 + 495 + 35	1136 + 356 + 35
m	24432	1559	998 + 495 + 2(35)	1136 + 356 + 2(35)
m	24463	1590	998 + 495 + 3(35)	1136 + 356 + 3(35)
m	24490	1617		
m	24532	1659		
m	24569	1696	998 + 2(356)	
w	24607	1734	998 + 2(356) + 35	
w	24635	1762	998 + 2(356) + 2(35)	
w	24671	1798	998 + 2(356) + 2(35)	1447 + 356
w	24696	1823		1447 + 356 + 35
w	24721	1848	998 + 495 + 356	1136 + 2(356)
w	24750	1877	998 + 495 + 356 + 35	1136 + 2(356) + 35
w	24779	1906	998 + 495 + 356 + 2(35)	1136 + 2(356) + 2(35)
w	24812	1939	1447 + 495	
w	24843	1970	1447 + 495 + 35	
w	24872	1999	2(998)	
w	24899	2026	2(998) + 35	
w	24932	2059	2(998) + 2(35)	
w	24958	2085	2(998) + 3(35)	
m	25008	2135	1136 + 998	
w	25041	2168	1136 + 998 + 35	
m	25075	2202	1136 + 998 + 2(35)	
w	25104	2231	1136 + 998 + 3(35)	
w	25130	2257		
w	25168	2295		
w	25193	2320		
vw	25225	2352	2(998) + 35	
vw	25254	2381		
w	25313	2440	1447 + 998	
w	25367	2494	1136 + 998 + 356	2(998) + 495
w	25433	2560		
w	25506	2633		
vw	25591	2718		
w	25735	2862		
w	25793	2920		
ms	25844	2971	2971	
w	25880	3007	2971 + 35	
m	25914	3041	2971 + 2(35)	
w	25948	3075	2971 + 3(35)	
w	25981	3108	2971 + 4(35)	
w	26118	3245		
w	26207	3334	2971 + 356	
vw	26342	3469	2971 + 495	
vw?	26431	3558		
w	26983	4110	2971 + 1136	
w	27017	4144	2971 + 1136 + 35	
w	27054	4181	2971 + 1136 + 2(35)	
vw	27323	4450	2971 + 1136 + 356	

[a] s = strong; m = medium; w = weak; v = very; c = continuum; ? = obscured.

The most striking feature of this transition is the prominence of a small interval of 35 cm.$^{-1}$ which adds on to most of the intense lines in the transition. The vibrational additions of the 35 cm.$^{-1}$ frequency show an alternation of intensity, with the 0, 2 and 4 quanta additions being stronger than the 1, 3 and 5 quanta additions.

Two lines appear weakly to the red of 22,873 cm.$^{-1}$, but these lines do not seem to be related to the rest of the transition, for reasons which will be given later. This transition has also been studied in a single crystal with a Wollaston prism. The weak lines appear in both polarized components and at 4°K. as well as at 20°K., and the spectra in the two different polarizations are essentially the same. The absorption is somewhat more intense in one polarization than in the other, although the lines at 23,871 and 23,941 cm.$^{-1}$ in Ac_2 show stronger absorption in the polarization in which the other lines are weaker. Some lines are depolarized. The dichroic splitting of the 22,873 cm.$^{-1}$ line was undetectably small (less than 2 cm.$^{-1}$). A small but detectable dichroic splitting of the lines at 23,871 and 23,941 cm.$^{-1}$ was observed, with the stronger component lying 4 ± 2 cm.$^{-1}$ to the red of the weaker component.

2.—An electronic–vibrational transition begins at 31,475 cm.$^{-1}$ (31,479 cm.$^{-1}$ in Ac_2-d_6) and is seen in a 0.5 mm. crystal. A microphotometer trace of this transition is shown in Fig. 2, and the vibrational analyses are given in Tables III and IV. The lines in this transition are much broader than the lines in the 22,873 cm.$^{-1}$ transition, and are about 30 cm.$^{-1}$ wide near the origin. The transition becomes increasingly diffuse toward higher energies and all vibrational structure is obliterated above 34,000 cm.$^{-1}$ as the discrete absorption merges into continuous absorption. Single crystals of thickness greater than 0.05 mm. could not be prepared by freezing the liquid, so that only the 22,873 cm.$^{-1}$ transition could be studied in single crystals.

TABLE II

VIBRATIONAL ANALYSIS OF STRONG VISIBLE ABSORPTION OF Ac_2-d_6 CRYSTAL (Crystal 0.025 mm.)

Int.	ν, cm.$^{-1}$	ν − 22896	Assignment	Assignment
w	22837	..	..	
vs	22896	0	$I\,^1A_u \leftarrow {}^1A_g$	
m	22934	38	35	
s	22966	70	2(35)	
m	23001	105	3(35)	
s	23034	138	4(35)	
m	23063	167	5(35)	
m	23090	194	194?	
m	23122	226	194 + 35	
m	23151	255	194 + 2(35)	
m	23183	287	194 + 3(35)	
s	23217	321	321	
w	23254	358	321 + 35	
m	23288	392	321 + 2(35)	
s	23360	464	464	
s	23389	493	464 + 35	
m	23426	530	464 + 2(35)	
m	23458	562	464 + 3(35)	
w	23511	615	464 + 4(35)	
w	23655	759		
s	23719	823	823	
w	23754	858	823 + 35	
m	23785	889	823 + 2(35)	
w	23820	924	823 + 3(35)	2(464)
m	23860	964	823 + 4(35)	
m	23934	1038		823 + 6(35)
w	23985	1089		
w	24014	1118		
s	24038	1142	823 + 321	1142
m	24087	1191	823 + 321 + 35	
m	24124	1228	823 + 321 + 2(35)	
m	24148	1252		
w	24182	1286	823 + 464	
w	24216	1320	823 + 464 + 35	
s	24320	1424	1424	
m	24354	1458	1424 + 35	
m	24388	1492	1424 + 2(35)	
m	24419	1523	1424 + 3(35)	
w	24448	1552	1424 + 4(35)	
w	24467	1571		
m	24499	1603	823 + 321 + 464	
m	24534	1638	823 + 321 + 464 + 35	2(823)
w	24568	1672	823 + 321 + 464 + 2(35)	
w	24602	1706	823 + 321 + 464 + 3(35)	
w	24641	1745		
m	24855	1959	2(823) + 321	
w	24889	1993	2(823) + 321 + 35	
m	24923	2027	2(823) + 321 + 2(35)	
w	24972	2076		
m	25132	2236	823 + 1424	
vw	25174	2278	823 + 1424 + 35	
w?	25210	2314	823 + 1424 + 2(35)	
w?	25277	2381		
?	25373	2477		
?	25464	2568		
w	25741	2845	2(1424)	
?	26095	3199		
?	26267	3371		
?	26688	3792		
?	26767	3871		
?	27421	4525		

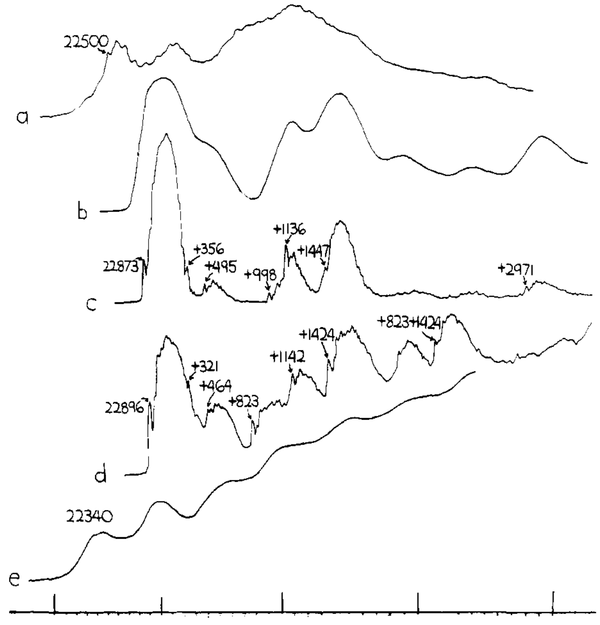

Fig. 1.—The strong blue absorption system of biacetyl: a, Ac_2 vapor, 300°K.; b, Ac_2 crystal, 77°K.; c, Ac_2 crystal, 4 or 20°K.; d, Ac_2-d_6 crystal, 4 or 20°K.; e, Ac_2 in 2-butanone crystal, 20°K.

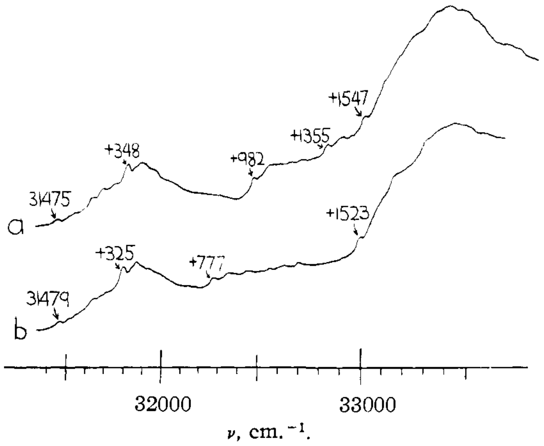

Fig. 2.—The ultraviolet absorption system of biacetyl: a, Ac_2 crystal, 20°K.; b, Ac_2-d_6 crystal, 20°K.

3.—An electronic–vibrational transition begins at 20,421 cm.$^{-1}$ (20,438 cm.$^{-1}$ in Ac_2-d_6) and is seen in a 0.5 mm. crystal. A microphotometer trace of this transition is shown in Fig. 3, and the vibrational analyses are given in Tables V and VI. The lines in this transition are as sharp as the lines in the 22,873 cm.$^{-1}$ transition. The 35 cm.$^{-1}$ frequency is prominent in long progressions in this transition. One very weak line appears to the red of the first line of this transition, at 20,355 cm.$^{-1}$ (20,376 cm.$^{-1}$ in Ac_2-d_6). This line will be important in interpreting the emission spectra. One other line in this transition does not appear to fit into the vibrational analysis, especially when it is compared with the corresponding lines in Ac_2-d_6. This line is at 22,359 cm.$^{-1}$ in Ac_2, and it shifts to 22,485 cm.$^{-1}$ in Ac_2-d_6.

The absorption spectra of biacetyl therefore show three electronic transitions with vibrational fine structure, and also show several lines which may belong to other electronic transitions.

B. Emission Spectra of Crystalline Biacetyl. 1.—An electronic–vibrational transition in the

TABLE III

VIBRATIONAL ANALYSIS OF ULTRAVIOLET ABSORPTION OF Ac_2 (Crystal 0.50 mm.)

Int.	ν, cm.$^{-1}$	ν − 31475	Assignment
w	31475	0	$II^1A_u \leftarrow {}^1A_g$
w	31547	72	2(36)
m	31640	165	165
m	31704	229	165 + 2(36)
vw?	31759	284	
vs	31823	348	348
m	31897	422	348 + 2(36)
w	31975	500	348 + 165
m	32189	714	2(348)
s	32457	982	982
m	32528	1053	982 + 2(36)
w	32718	1243	
m	32830	1355	1355
m	32911	1436	1355 + 2(36)
m	33022	1547	1547
m	33097	1622	1547 + 2(36)
s c	33229	1754	
s c	33356	1881	1547 + 348
s c	33710	2235	
m c	33938	2463	
s c	33999	2524	982 + 1547
s c	>34000		

TABLE IV

VIBRATIONAL ANALYSIS OF ULTRAVIOLET ABSORPTION OF Ac_2-d_6 CRYSTAL (Crystal 0.50 mm.)

Int.	ν, cm.$^{-1}$	ν − 31479	Assignment
w	31479	0	$II^1A_u \leftarrow {}^1A_g$
vw	31560	81	2(40)
w	31654	175	175
vw	31733	254	175 + 2(40)
s	31804	325	325
m	31801	402	325 + 2(40)
w	31951	472	325 + 4(40)
m	32256	777	777
w	32334	855	777 + 2(40)
m	32635	1156	1156
s	33002	1523	1523
s	33081	1602	1523 + 2(40)
s c	33329	1850	1523 + 325
s c	33395	1916	1523 + 335 + 2(40)
s c	33479	2000	1523 + 325 + 4(40)
s c	>34000		

TABLE V

VIBRATIONAL ANALYSIS OF WEAK VISIBLE ABSORPTION OF Ac_2 CRYSTAL (Crystal 0.50 mm.)

Int.	ν, cm.$^{-1}$	ν − 20,421	Assignment	Assignment
w	20355	. .	?	
vs	20421	0	$I^3A_u \leftarrow {}^1A_g$	
m c	20460	39	35	
vs	20492	71	2(35)	
m	20528	107	3(35)	
s c	30562	141	4(35)	
m	20779	358	358	
vw	20817	396	358 + 35	
m	20851	430	358 + 2(35)	
vw	20880	459	358 + 3(35)	
w	20915	494	358 + 4(35)	
vw	20948	527	358 + 5(35)	
vw	20979	558	358 + 6(35)	
vw	21014	593	358 + 7(35)	
vw?	21127	706	2(358)	
vw?	21378	957		
m	21430	1009	1009	
w	21504	1083	1009 + 2(35)	3(358)
s	21565	1144	1144	
w	21603	1182	1144 + 35	
m	21635	1214	1144 + 2(35)	
w	21670	1249	1144 + 3(35)	
m	21890	1469	1469	
m	21926	1505	1469 + 35	1144 + 358
w	21965	1544	1469 + 2(35)	
w	22000	1579	1469 + 3(35)	
vs	22172	1751	1751	
m	22203	1782	1751 + 35	
s	22245	1824	1751 + 2(35)	
vs	22359	. .	$I^1B_g \leftarrow {}^1A_g$?	

TABLE VI

VIBRATIONAL ANALYSIS OF WEAK VISIBLE ABSORPTION OF Ac_2-d_6 CRYSTAL (Crystal 0.50 mm.)

Int.	ν, cm.$^{-1}$	ν − 20438	Assignment
w	20375	. .	?
vs	20438	0	$I^3A_u \leftarrow {}^1A_g$
m	20475	37	35
s	20505	67	2(35)
w	20536	98	3(35)
m	20573	135	4(35)
s	20763	325	325
w	20803	365	325 + 35
m	20842	404	325 + 2(35)
w	20923	485	325 + 4(35)
vw	21082	644	2(325)
w	21263	825	825
vw?	21408	970	3(325)
vw	21486	1048	3(325) + 2(35)
s	21586	1148	1148
w	21622	1184	1148 + 35
m	21657	1219	1148 + 2(35)
vw	21691	1253	1148 + 3(35)
w	21725	1287	4(325)
m	21908	1470	1148 + 325
vw	21943	1505	1148 + 325 + 35
w	21980	1542	1148 + 325 + 2(35)
w	22073	1635	2(825)
s	22187	1749	1749
w	22223	1785	1749 + 35
m	22265	1827	1749 + 2(35)
w	22303	1865	1749 + 3(35)
s	22485	. .	$I^1B_g \leftarrow {}^1A_g$?

green and red regions of the spectrum is seen when a 0.025 mm. biacetyl crystal is illuminated with the blue or purple line from a high pressure mercury arc. This emission, which appears green to the eye, has been studied by many workers.[12] In the crystal, it appears to consist of sharp lines superimposed on a background which shows broad structure. With the apparatus employed in these experiments, the intense green emission spectrum could be photographed in five to ten minutes. The first line (line of highest energy) is a very intense, sharp line at 19,806 cm.$^{-1}$ (19,996 cm.$^{-1}$ in Ac_2-d_6). This line did not appear at all in absorption, even when a three mm. polycrystalline mass was used in recording the absorption spectrum. A deep yellow filter, Corning 3385, was placed between the source

(12) See N. A. Coward and W. A. Noyes, *J. Chem. Phys.*, **22**, 1207 (1954), for previous references.

TABLE VII

VIBRATIONAL ANALYSIS OF STRONG GREEN EMISSION Ac_2 CRYSTAL (T = 4°K.; crystal 0.025 mm.)

Int.	ν, cm.⁻¹	19806 − ν	Assignment	Assignment
vvs	19806	0	?	
s	19762	44	35	
vs	19739	67	2(35)	
vs	19720	86	3(35)	
vs c	19661	145	4(35)	
m c	19450	356		
vs	19420	386	386?	
s c	19338	468		
m c	19276	530		
m c	19201	605		
s	19114	692	2(347)?	
w	19079	727	2(347) + 35	
m	19039	767	2(347) + 2(35)	2(386)
m	18962	843	2(347) + 4(35)	
w	18870	936		
w	18765	1041		
w	18712	1094		
w	18624	1182		
w	18595	1211		
w	18559	1247		
vs	18520	1280	1280	
m	18493	1313	1280 + 35	
s	18461	1345	1280 + 2(35)	
m	18424	1382	1280 + 3(35)	4(347)
s	18395	1411	1280 + 4(35)	
s c	18376	1430		
vs	18089	1717	1717	
m	18047	1759	1717 + 35	
vs	18012	1794	1717 + 2(35)	
vs c	17944	1862	1717 + 4(35)	
vs c	17836	1970	2(347) + 1280	
vs c	17764	2042	2(347) + 1280 + 2(35)	
m c	17698	2108	1717 + 386	
w c	17617	2189	1717 + 386 + 2(35)	
w c	17536	2270		
m	17398	2408	2(347) + 1717	
m	17328	2478	2(347) + 1717 + 2(35)	
w	17293	2513	2(347) + 1717 + 3(35)	
m	17257	2549	2(1280)	
m	17221	2585	2(1280) + 35	
w	17189	2617	2(1280) + 2(35)	
m	17114	2692		
m c	17038	2768		
w c	16868	2938	2(1280) + 386	
w c	16843	2963		
s	16810	2996	1280 + 1717	
w	16779	3027	1280 + 1717 + 35	
s	16743	3063	1280 + 1717 + 2(35)	
s c	16672	3134	1280 + 1717 + 4(35)	
s c	16575	3231		
s c	16495	3311		
m	16380	3426	2(1717)	
m c	16308	3498	2(1717) + 2(35)	
m c	16220	3586		
w c	16122	3684		
w	16059	3747		
w	15988	3818		
w	15914	3892		
vw	15683	4123		
vw	15607	4199		
w	15543	4263	2(1280) + 1717	
w	15471	4335	2(1280) + 1717 + 2(35)	
w c	15393	4413		
vw	15104	4702	2(1717) + 1280	
vw	15045	4761	2(1717) + 1280 + 2(35)	
vw	14963	4843		

TABLE VIIIa

VIBRATIONAL ANALYSIS OF STRONG GREEN EMISSION OF Ac_2-d_6 CRYSTAL (T = 4°K.; crystal 0.025 mm.)

Int.	ν, cm.⁻¹	19996 − ν	Assignment	Assignment
vs	19996	0	?	
m	19958	38	35	
s	19929	67	2(35)	
m	19900	96	3(35)	
s	19841	155		
vs	19819	177		
vs c	19756	240		
vs c	19678	318		
vs c	19636	360		
vs c	19597	399		
vs c	19514	482		
s c	19472	524		
s	19408	588		
s	19333	663		
w? c	19246	747		
m c	19147	849		
m c	19055	941		
m c	18983	1013		
m	18883	1113		
m	18736	1260		
s	18697	1299	1299	
w	18661	1335	1299 + 35	
m	18630	1366	1299 + 2(35)	
m	18542	1454		
m	18515	1481		
m c	18485	1511		
s c	18457	1539		
s c	18382	1614		
vs	18280	1716	1716	
m c	18247	1749	1716 + 35	
m c	18213	1783	1716 + 2(35)	
m	18172	1824	1716 + 3(35)	
m	18123	1873		
m	18107	1889		
vs c	18046	1950		
s c	17970	2026		
s c	17887	2109		
s c	17766	2230		
m	17427	2569		
m	17407	2589	2(1299)	
m c	17348	2648		
m	17224	2772		
m c	17173	2823		
m c	17095	2901		
m c	17013	2983		
m	16985	3011	1299 + 1716	
w	16918	3078	1299 + 1716 + 2(35)	
w	16802	3194		
m c	16747	3249		
m c	16668	3328		
w c	16573	3423	2(1716)	

TABLE VIIIb

VIBRATIONAL ANALYSIS OF THE BROAD MAXIMA IN THE STRONG GREEN EMISSION OF Ac_2 AND Ac_2-d_6 CRYSTAL

Int.	$\nu \pm 50$	$19660 - \nu$	Assignment
vs	19660	0	?
s	18320	1340	1280 (or 1300), ν_2
s	17890	1770	1730, ν_1
m	17060	2600	2(1280)
m	16550	3110	1730 + 1280
w	16180	3480	2(1730)
vw	15740	3920	3(1280)
vw	15360	4300	1730 + 2(1280)

and the crystal to remove all source energies higher than 20,440 cm.$^{-1}$. This was done to prevent emission of 19,806 cm.$^{-1}$ which might obscure any absorption, but no absorption of 19,806 cm.$^{-1}$ could be detected.

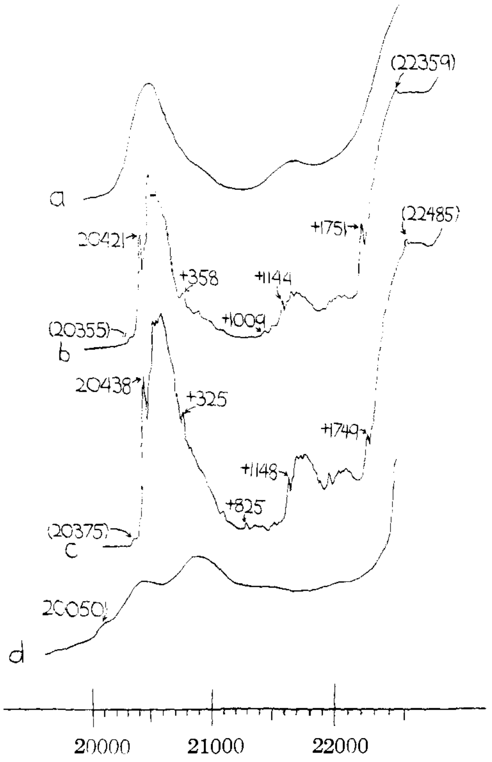

Fig. 3.—The weak blue absorption system of biacetyl: a, Ac_2 crystal, 77° K.; b, Ac_2 crystal, 4 or 20°K.; c, Ac_2-d_6 crystal, 4 or 20°K.; d, Ac_2 in 2-butanone crystal, 20°K.

Microphotometer traces of this transition are shown in Fig. 4, and vibrational analyses are given in Tables VII and VIIIa and VIIIb. Although the sharp lines all shift to the violet on deuteration, the broad maxima of the continuous emission do not shift, within the limit of observation of approximately 30 cm.$^{-1}$. The 35 cm.$^{-1}$ frequency is prominent in this transition, and it hows the same alternation of intensity which was previously mentioned.

2.—If the emission of biacetyl at 4°K. is photographed for one to two hours with the same arrangement used to photograph the intense green emission, then several very sharp emission lines appear to the violet of the first strong line at 19,806 cm.$^{-1}$ (19,996 cm.$^{-1}$ in Ac_2-d_6). The line of highest energy, which appears faintly, is at 20,355 cm.$^{-1}$ in Ac_2 and 20,376 cm.$^{-1}$ in Ac_2-d_6, and therefore coincides within the limit of error (4 cm.$^{-1}$) with the very weak lowest energy absorption line in biacetyl crystal. The lines in this weak green emission transition are listed in Tables IX and X.

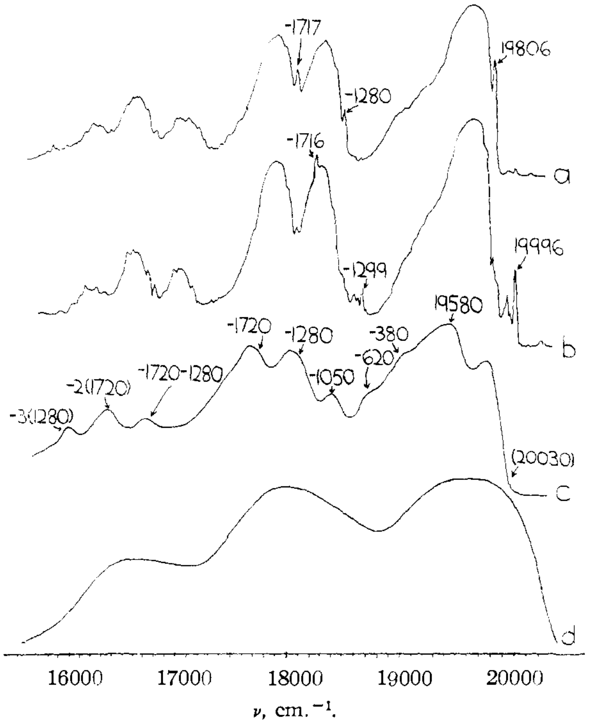

Fig. 4.—The strong green emission system of biacetyl: a, Ac_2 crystal, 4°K.; b, Ac_2-d_6 crystal, 4°K.; c, Ac_2 (or Ac_2-d_6) in 2-butanone crystal, 20°K.; d, Ac_2 in 2-butanone glass, 20°K.

TABLE IX

WEAK GREEN EMISSION OF Ac_2

T = 4°K.

Int.	ν, cm.$^{-1}$	$20355 - \nu$	Assignment
vw	20355	0	?
w	20327	28	
w	20294	61	
vw	20259	96	
m	20236	119	
vw	20217	138	
w	20204	151	
w	20179	176	
w	20148	207	
s	20119	236	
w	20111	244	
w	20073	282	
m	20028	327	
vs	19991	364	
w	19965	390	
w doubled	19926	429	
w	19891	464	
s	19839	516	

3.—A two-hour exposure of the emission of biacetyl crystal at 4°K. also shows at higher energies a very weak series of lines belonging to another

TABLE X

WEAK GREEN EMISSION OF Ac_2-d_6

$T = 4°K.$

Int.	ν, cm.$^{-1}$	20376 − ν	Assignment
w	20376	0	?
m	20343	33	
m	20313	63	
m	20274	102	
m	20194	182	
s doubled slightly	20126	250	
w	20086	290	
s doubled	20036	340	
vs} in strong	19841	535	
vs} green emission	19819	557	
vs	19756	620	

electronic-vibrational emission transition. The highest energy emission in this series of lines occurs within 3 cm.$^{-1}$ of the strong absorption line at 22,873 cm.$^{-1}$. The line at 22,873 cm.$^{-1}$ does not appear because the absorption coefficient at 22,873 cm.$^{-1}$ is greater than at the exciting line, so that 22,873 is reabsorbed. This very weak blue emission transition has been previously detected in biacetyl vapor,[12] although no vibrational analysis has been proposed. A microphotometer trace of this transition (medium Hilger Spectrograph) is shown in Fig. 5, and vibrational analyses are listed in Tables XI and XII.

TABLE XI

VIBRATIONAL ANALYSIS OF VERY WEAK BLUE EMISSION OF Ac_2 CRYSTAL ($T = 4°K.$)

Int.	ν, cm.$^{-1}$	22873 − ν	Assignment
[a]	22873	0	$I^1A_u \rightarrow {}^1A_g$
m, c	22766	107	3(35)
s	22493	380	380
m	22436	437	380 + 2(35)
w	22388	485	380 + 3(35)
s	22256	617	617
m	22188	685	617 + 2(35)
m	21861	1012	617 + 380
s	21817	1056	1056
w	21785	1088	1056 + 35
m	21751	1122	1056 + 2(35)
w	21695	1179	
s	21589	1284	1284
w	21550	1323	1284 + 35
s	21505	1368	1284 + 2(35)
w	21465	1408	
m	21427	1446	1056 + 380
s	21144	1729	1729

[a] Violet edge of continuum.

TABLE XII

VIBRATIONAL ANALYSIS OF VERY WEAK BLUE EMISSION OF Ac_2-d_6 CRYSTAL ($T = 4°K.$)

Int.	ν, cm.$^{-1}$	22896 − ν	Assignment
[a]	22896	0	$I^1A_u \rightarrow {}^1A_g$
s	22552	344	344
s	21943	953	953
s	21590	1306	1306 (344 + 953)
s	21249	1647	1306 + 344
s	21168	1728	1728

[a] Violet edge of continuum.

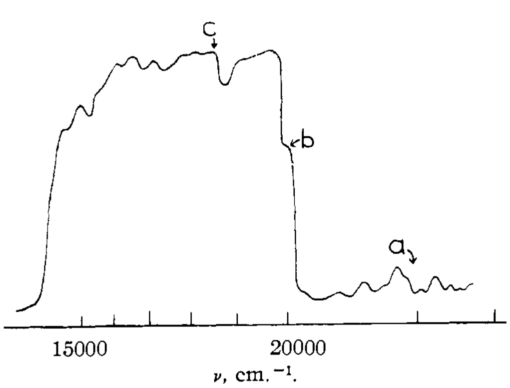

Fig. 5.—Emission spectrum of Ac_2 crystal, 20°K., medium Hilger spectrograph: a, very weak blue emission system; b, weak green emission system; c, strong green emission system.

Thus, there are at least two electronic-vibrational emission transitions, and in addition there are several sharp lines to the violet of the strong green emission transition.

C. Spectra of Biacetyl in 2-Butanone.—The spectra of biacetyl and biacetyl-d_6 were also studied in solid solution in 2-butanone. Solutions were prepared by mixing biacetyl and 2-butanone and slowly freezing the mixture. Rapid freezing by direct immersion into liquid nitrogen often resulted in a glassy solution, but slow freezing of solutions containing less than 25% biacetyl resulted in a crystalline solution. Solutions containing more than 30% biacetyl always gave a glass, even on slow freezing. The spectra of biacetyl in 2-butanone crystal at 20°K. are much broader than the spectra of crystalline biacetyl, and vibrational fine structure could be only partially analyzed. The emission spectra in 2-butanone show the strong green, weak green and very weak blue emission transitions, although the intensity of the weak green emission relative to the strong green emission is greatly enhanced in solid solution. The absorption spectra in 2-butanone also show the weak and strong absorption transitions in the blue region, although the spectra are not sharp enough to detect the possible presence of the weaker lines to the red of each of these transitions. The absorption in the ultraviolet could not be investigated, since the 2-butanone absorbs at the same energy as the ultraviolet absorption of biacetyl.

Microphotometr traces of the transitions are shown in Figs. 1, 3 and 4, and vibrational analysis of the strong green emission transition is listed in Table XIII. In 2-butanone, the spectra of biacetyl and biacetyl-d_6 are so broad that they cannot be distinguished.

The spectra of biacetyl in 2-methylbutadiene, 2,3-dimethylbutadiene, and tetramethylethylene were not as sharp as those in 2-butanone, and are not reported here.[13]

IV. Interpretations of the Electronic Transitions

The number and nature of the electronic transitions will be discussed here, and the vibrational fine structure will be discussed in detail in paper II.

---

[13] Thanks are due to Dr. D. C. Smith of Phillips Petroleum Co. for generous gifts of the hydrocarbons used in these experiments.

1.—The absorption transition beginning at 22,873 cm.$^{-1}$ certainly corresponds to the very weak blue emission transition beginning just to the red of 22,873 cm.$^{-1}$ (22,896 cm.$^{-1}$ in Ac$_2$-d_6). The weaker lines at 22,805 and 22,845 cm.$^{-1}$ (22,837 cm.$^{-1}$ in Ac$_2$-d_6) appear as absorption lines on the weak continuous emission background originating from 22,873, and therefore do not belong to this electronic–vibrational transition. These weaker lines are not "hot" lines, since they appear in absorption at 4°K. as well as at 20°K. Since the absorption and emission transitions originate from the same line, the electronic transition is allowed by symmetry. The corresponding electronic transition has been studied in glyoxal vapor by Brand,[14] who also finds that the corresponding O–O band at 21,977 cm.$^{-1}$ in (CHO)$_2$ (22,016 cm.$^{-1}$ in (DCO)$_2$) is allowed by symmetry, since it appears strongly in both absorption and fluorescence. From a rotational analysis of the O–O band, Brand has concluded that the transition moment lies along the twofold symmetry axis. This is in agreement with the LCAO–MO prediction that the lowest allowed n-π^* transition in glyoxal and biacetyl should be I^{1}A$_u$ – ^{1}A$_g$. The absorption transition is quite weak ($\epsilon \cong 20$) but is fully allowed. It will be shown in II that most of the vibrational fine structure is best interpreted as additions of a$_g$ modes to the O–O line.

The transition energies of the I^{1}A$_u$–^{1}A$_g$ transition in several media are compared in Table XIV. The exact location of the O–O transition in the vapor is uncertain, and the O–O transitions in the other media are broad.

TABLE XIII

VIBRATIONAL ANALYSIS OF CONTINUOUS MAXIMA IN STRONG GREEN EMISSION OF Ac$_2$ (AND Ac$_2$-d_6) IN 2-BUTANONE CRYSTAL

Int.	$\nu \pm 40$, cm.$^{-1}$	$19580 - \nu$	Assignment
m	20035	..	"Weak" green emission
vs	19580	0	I^{3}B$_g$ → ^{1}A$_g$?
s	19220	360	ν_5
m	18930	650	ν_4
s	18570	1010	ν_3
vs	18240	1340	ν_2
vs	17840	1740	ν_1
m	16550	3030	$\nu_2 + \nu_1$
w	16150	3430	$2\nu_1$
vw	15620	3960	$3\nu_2$
vw	15190	4390	$2\nu_2 + \nu_1$

TABLE XIV

THE I^{1}A$_u$–^{1}A$_g$ AND I^{3}A$_u$–^{1}A$_g$ TRANSITIONS IN VARIOUS MEDIA

Medium	ν, cm.$^{-1}$
I^{1}A$_u$–^{1}A$_g$	
Vapor, 300°K.	22500 ?
Crystal, 20°K.	22873 ± 4
2-Butanone crystal, 20°K.	22340 ± 40
2-Butanone glass, 20°K.	23300 ± 300
I^{3}A$_u$–^{1}A$_g$	
Crystal, 20°K.	20421 ± 4
2-Butanone crystal, 20°K.	20055 ± 40

The vibrational analysis of this absorption transition shows no evidence for supposing it to consist of two electronic transitions. This is contrary to the conclusions of Lewis and Kasha,[10] and of Forster.[11] All of the lines can be well accounted for in the vibrational analysis originating from the first line at 22,873 cm.$^{-1}$ in crystalline biacetyl.

The absorption spectra of single crystals of biacetyl in this region do not show evidence of any great effect of the solid state on the transition. The envelope of the transition is similar in the crystal and in the vapor states. The transition in the crystal is shifted by less than 2% toward higher energies compared to the vapor. Dichroic splittings, which are characteristic of one effect of the crystalline lattice on the molecular transition,[15] are either only 4 ± 2 cm.$^{-1}$ or undetectably small (<2 cm.$^{-1}$). The weak lines to the red of the O–O line may be due to crystal effects, but the emission originates from the origin of the absorption at 22,873 cm.$^{-1}$, so that there is no doubt that 22,873 is the O–O line. In conclusion, this transition does not seem to show any great evidence of crystalline perturbations, and it is therefore considered a good approximation to classify the electronic–vibrational spectra of crystalline biacetyl in terms of the symmetry of the free molecule.

2.—The absorption transition beginning at 31,475 cm.$^{-1}$ is much broader than the absorption transition beginning at 22,873 cm.$^{-1}$. This is attributed to predissociation of the molecule in the upper electronic state, and is related to the fact that biacetyl undergoes photochemical reactions when illuminated in this absorption band.[16]

The vibrational fine structure is also in agreement with an unstable upper state. The O–O "line" at 31,475 cm.$^{-1}$ is not one of the most prominent lines in this transition, in contrast with the O–O line at 22,873 cm.$^{-1}$, which is one of the most prominent lines in the I^{1}A$_u$–^{1}A$_g$ transition. The intensity of this transition increases toward higher energies, indicating that the dimensions of upper and lower states must differ considerably. In agreement with McMurry,[5] this transition is assigned to a n-π^* transition, II^{1}A$_u$–^{1}A$_g$.

3.—The absorption transition beginning at 20,421 cm.$^{-1}$ must now be discussed in relation to the weak and strong green emission transitions. It has long been expected that there should be a weak absorption transition in this region.[17] However, the weak absorption transition originating from 20,421 cm.$^{-1}$ cannot correspond to the same electronic–vibrational transition as the strong green emission transition, since 20,421 does not appear in emission from a 0.025 mm. crystal when it is illuminated with λ 4047 Å. Hg. Reabsorption is not the answer here, since the absorption at 20,421 cm.$^{-1}$ does not show up at all in a 0.025 mm. crystal, and appears only weakly in a 0.25 mm. crystal. The line of highest energy in the strong green emission is at 19,806 cm.$^{-1}$ (19,996 cm.$^{-1}$ in Ac$_2$-d_6), so that there is a considerable gap between the origins of the weak absorption and strong green emission.

---

(14) J. C. D. Brand, *Trans. Faraday Soc.*, **50**, 431 (1954).

(15) A. S. Davydov, *J. Exptl. Theoret. Phys. U.S.S.R.*, **18**, 210 (1948).

(16) See G. F. Sheats and W. A. Noyes, THIS JOURNAL, **77**, 1421 (1955), for previous references.

(17) G. M. Almy and S. Anderson, *J. Chem. Phys.*, **8**, 805 (1940).

The one very weak line at 20,355 cm.$^{-1}$ (20,376 cm.$^{-1}$ in Ac$_2$-d_6) is the only line in this region which appears in both absorption and emission, and it is possibly the O–O line of some electronic transition. The sharp lines in the weak green emission originate from this line, but it has not been possible to successfully analyze these lines. It is not yet certain whether the strong green emission belongs to the same electronic transition as the weak green emission, since the gaps of 549 ± 6 cm.$^{-1}$ in Ac$_2$ and 380 ± 6 cm.$^{-1}$ in Ac$_2$-d_6 do not correspond to any known vibrational frequencies of biacetyl. All attempts to find the strong green emission line at 19,806 cm.$^{-1}$ (19,996 cm.$^{-1}$ in Ac$_2$-d_6) in absorption have failed.

Another puzzling phenomenon is the fact that the broad maxima in the strong green emission do not shift on deuteration, whereas the sharp lines in the strong green emission shift approximately 190 cm.$^{-1}$ to the violet. It is therefore possible to discuss the appearance of the green emission spectrum in at least two ways. On the basis of intensity, it consists of a weak green emission at slightly higher energies than the strong green emission. On the basis of sharpness, it consists of sharp lines and broad bands. The sharp lines in both the weak and strong green emission transitions shift with deuteration, whereas the broad bands do not shift with deuteration. The emission spectra of crystalline biacetyl in this region are therefore quite complex, and a complete interpretation cannot be given at the present time.

A tentative assignment of the spectra will now be given. The weak absorption system originating from 20,421 cm.$^{-1}$ (20,437 cm.$^{-1}$ in Ac$_2$-d_6) is assigned to a singlet–triplet absorption transition. Since no emission arises from 20,421, it is not possible to prove whether or not this transition is allowed by symmetry. It is probable that 20,421 is the O–O line of one electronic transition, but that there is also a still lower excited electronic state which gives rise to the green emission. The spectra of biacetyl in crystalline 2-butanone clearly show a gap of 460 ± 60 cm.$^{-1}$ between the origins of the weak absorption and strong green emission. In the crystalline solid solution, as in the pure crystal, the weak green emission, which is considerably intensified in the solid solution, appears to the violet of the strong green emission. This also appears in the vapor, although the lines are so broad in the vapor that a direct comparison is less certain. The gap shown between the weak absorption and strong green emission may be due to a symmetry prohibition of the O–O line if the weak absorption and strong green emission do correspond to the same electronic transition, which would then be a I^{3}B$_g$–^{1}A$_g$ transition. However, this explanation would fail to account for the appearance of the weak green emission. The authors therefore feel that at least two electronic transitions are needed to account for the complexity of both the strong and weak green emission spectra of biacetyl.

This complication does not arise in glyoxal vapor.[14] The O–O band of the I^{3}A$_u$ – ^{1}A$_g$ transition at 19,197 cm.$^{-1}$ appears in both absorption and emission in (DCO)$_2$ and the gap between emission and absorption found in biacetyl does not occur in glyoxal. However, it is known that the CH$_3$ groups must have some effect on the electronic transitions of these molecules, since the emission in (CHO)$_2$ is predominantly blue (singlet–singlet) whereas the emission in (CH$_3$CO)$_2$ is predominantly green (triplet–singlet), so that the spectra may not be comparable in all details.

The absorption line at 20,421 cm.$^{-1}$ is therefore assigned to the O–O line of the I^{3}A$_u$–^{1}A$_g$ electronic transition, and another triplet level, the ^{3}B$_g$ state, must be responsible for the emission spectrum. The radiationless conversion from ^{3}A$_u$ to ^{3}B$_g$ must be assumed to be 100% efficient.

The location of the ^{3}B$_g$ state must now be considered. The line at 20,355 may be the O–O line. If so, its appearance is induced by the unsymmetrical environment of the crystal. The other weak green emission lines are perhaps also crystal induced. On this assumption, the strong green emission would have to be vibrationally induced. However, the interval from 20,355 to the first strong emission line would then correspond to a non-totally symmetric ground state interval and we have not been able to identify it with one. This interval is 549 in Ac$_2$ and 380 in Ac$_2$-d_6. The difficulties may be connected with a possible change in the geometry of the molecule in going from the I^{1}A$_g$ to the I^{3}B$_g$ state. A twisting about the central C–C bond, for example, could lead to a very complicated spectrum.

The separation between the singlet and triplet states arising from the first excited n-π^* configuration of glyoxal or biacetyl is 2500–3000 cm.$^{-1}$, which is considerably greater than the value previously predicted by Reid.[18]

4.—The vibrational analysis of the I^{3}A$_u$–^{1}A$_g$ absorption transition shows one line which shifts in an anomalous manner upon deuteration. This line, which is prominent in this region although it is partly obscured by diffuse absorption, lies at 22,359 cm.$^{-1}$ in Ac$_2$, and shifts to 22,485 cm.$^{-1}$ in Ac$_2$-d_6. The intervals from the origin of the weak absorption at 20,421 (20,438) are 1938 cm.$^{-1}$ in Ac$_2$ and 2047 cm.$^{-1}$ in Ac$_2$-d_6. No vibrational fundamental frequency of Ac$_2$ is expected to occur at 1938 cm.$^{-1}$. Although this interval may correspond to a combination or overtone, the large *increase* of the frequency on deuteration is anomalous. It is tentatively suggested that this line may be the O–O line of the I^{1}B$_g$–^{1}A$_g$ transition, which is predicted by MO theory, and that it appears because of environmental effects. This explanation would be ruled out if the crystallographic space group possessed a center of symmetry, although a distortion of the upper state might also allow the forbidden O–O line to appear. This assignment is in qualitative agreement with the violet shift of this line on deuteration, since the O–O lines of the other electronic transitions also shift to the violet on deuteration, but the magnitude (109 cm.$^{-1}$) of this shift is considerably greater than for the I^{1}A$_u$–^{1}A$_g$ transition (23 cm.$^{-1}$) or for the I^{3}A$_u$–^{1}A$_g$ transition (17 cm.$^{-1}$). The assignment of the 22,359 cm.$^{-1}$ absorption line in Ac$_2$ (22,485 cm.$^{-1}$ in Ac$_2$-d_6) to the

---

(18) C. Reid, *J. Chem. Phys.*, **21**, 1906 (1953).

O–O line of the I^{1}B$_g$–^{1}A$_g$ transition is therefore only tentative. The weak lines to the red of the ^{1}A$_u$–^{1}A$_g$ O–O line, namely, 22,845 and 22,805 (22,837 in *d*-6), may be connected with the ^{1}B$_g$ state. The transition to this state would be vibrationally induced, and both the strength of these lines and their position are compatible with the theoretical requirements for a skeletal u-vibration in a forbidden transition.

V. Conclusions

The one-electron LCAO-MO's for biacetyl are shown in Fig. 6, and the states derived from them are shown schematically in Fig. 7. The observed electronic states are listed in Table XV.

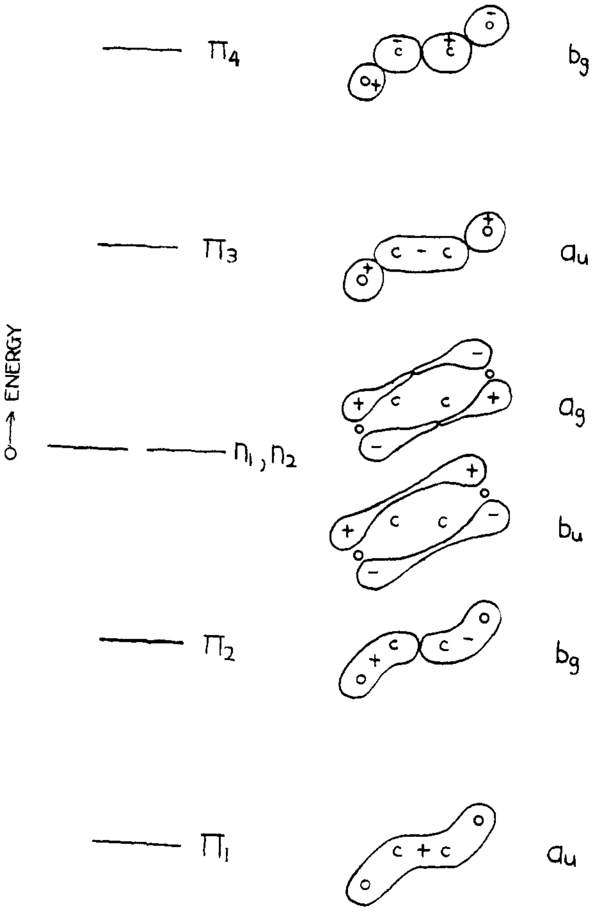

Fig. 6.—Molecular orbitals for biacetyl. Only the n and π orbitals are shown. The σ bonding orbitals lie below π_1 and the σ antibonding orbitals lie above π_4.

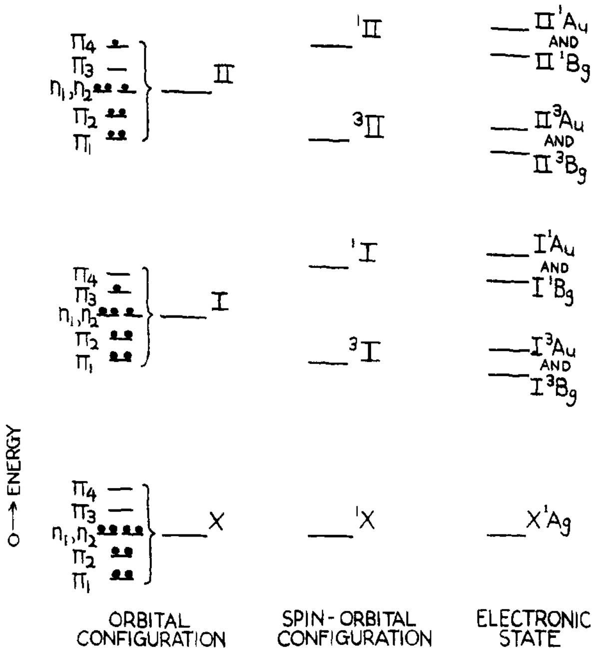

Fig. 7.—The n, π configurations and states for biacetyl.

TABLE XV

ELECTRONIC ENERGIES (CM.$^{-1}$) OF Ac$_2$ AND Ac$_2$-d_6, CRYSTALLINE STATE (^{1}A$_g$ = 0)

	Ac$_2$	Ac$_2$-d_6
I^{3}B$_g$	>19700 <20355	>19700 <20376
I^{3}A$_u$	20421	20438
I^{1}B$_g$	22359 ?	22485 ?
I^{1}A$_u$	22873	22896
II^{1}A$_u$	31475	31479

The electronic–vibrational spectra of biacetyl at low temperatures in the crystalline state and in crystalline solid solution have yielded more detailed information than the spectra in the vapor or in solution at room temperature, due to the increase in sharpness. The long wave length n-π^* transitions have been vibrationally analyzed, and the electronic transitions have been interpreted in terms of the LCAO-MO theory. The I^{1}A$_u$ and I^{3}A$_u$ states are similar to the ground ^{1}A$_g$ state in dimensions, whereas the II^{1}A$_u$ state predissociates. Spectral evidence for the presence of the I^{1}B$_g$ and I^{3}B$_g$ states is also presented.

BERKELEY, CAL.