

## InfraRed Absorption Spectra at Low Temperatures

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With this approximation and using the values of Parr and Crawford,<sup>6</sup> we obtain as a value for  $\alpha = 4.20$  ev and for  $\beta_{12}' = 2.42$  ev.

The only experimental data we have used are the effective nuclear charge for a C atom  $Z = 3.18^6$  and the C—C distance 1.39 Å in benzene.<sup>7</sup> In the calculation of  $\alpha$  we used for  $W2p$ , the energy of a  $2p$ -electron in the unexcited carbon atom, instead of the experimental ionization potential of  $-11.24$  ev, a value of  $-10.82$  ev calculated theoretically with the effective nuclear charge of 3.18;  $\beta_{12}'$  is independent of  $W2p$ .

From these and analogous calculations we conclude:

(1)  $\beta_{12}'$  is with good approximation, independent of the potential field of the  $r$ -electrons (the term  $V_r \cdot S_{12}$  cancels).

(2) For a definite C—C bond  $\beta_{12}'$  is proportional to  $S_{12}$ . This was already known from empirical data.<sup>8</sup>

(3)  $\beta_{12}'$  is strongly dependent on the environment of the bond in the molecule (e.g., for naphthalene  $\beta_{12}' = -1.93$  ev and  $\beta_{910}' = -2.26$  ev).

(4) The quantitative results of the molecular orbital method are improved if we consider as a second approximation also the exchange and lack of orthogonality integrals between non-adjacent atoms. Following our method with  $a$ , for this correction reasonable approximation, we obtain for benzene

$$\beta_{13}' = \frac{S_{13}}{S_{12}} \beta_{12}'; \quad \beta_{14}' = \frac{S_{14}}{S_{12}} \beta_{12}',$$

$$(S_{12} = 0.26; \quad S_{13} = 0.04; \quad S_{14} = 0.02).$$

In this second approximation we compute for the resonance energy (R.E.) of benzene,  $0.76\beta_{12}'$  (zero-approximation R.E.  $2\beta_{12}$ , first-approximation R.E.  $1.06\beta_{12}'$ ). With the experimental value for the R.E. (39 kcal.<sup>9</sup>), we compute for  $\beta_{12}' = -2.23$  ev. The calculated R.E. with our theoretical value for  $\beta_{12}'$  is 42 kcal.

For the energy difference  $\Delta E$  between the ground state and the first excited state we evaluate in second approximation  $2.14\beta_{12}'$ , which gives 2410 Å with our theoretical value of  $-2.42$  ev as compared with the experimental value of 2550 Å.

For the quantity  $\Delta E/\text{R.E.}$ , which is independent of  $\beta_{12}'$ , we obtain experimentally, 2.86; calculated, 2.82. Thus the well-known discrepancy between the spectroscopical and the thermochemical value is eliminated in our second approximation.

For ethene we find with the same method ( $S_{12} = 0.287$ )  $\beta_{12}' = -2.95$  ev, in agreement with the experimental spectroscopical value  $\beta_{12}' = -3.0$  ev<sup>10</sup> (They are, however, not strictly comparable.) The theoretical value for  $\alpha$  is 8.0 ev.

For naphthalene, we compute in second approximation, R.E. is  $1.22\beta_{12}'$ ; for anthracene,  $1.61\beta_{12}'$ . We have taken into account  $\beta_{13}'$ ,  $S_{13}$  etc., but  $\beta_{12}'$ , contrary to our third conclusion, was not varied with the environment in the molecule.

For the ultraviolet spectrum, we obtain with the calculated values of  $\Delta E/\text{R.E.}$  with the experimental values of R.E.<sup>9</sup>

	0° approx.	1° approx.	2° approx.	obs.
benzene	7143 Å	3630 Å	2600 Å	2550 Å
naphthalene	11,430 Å	5461 Å	3524 Å	2750 Å
anthracene	17,212 Å	8236 Å	5037 Å	3800 Å

A further improvement might be obtained from a variation of  $\beta_{12}'$ .

If this method leads to reasonable results it will, in the future, be possible to calculate  $\beta_{12}'$  for an arbitrary bond in a molecule by a simple addition if we know the internuclear distances of that molecule, and to expand this method, e.g., to heterocyclic molecules.

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## Infra-Red Absorption Spectra at Low Temperatures\*

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October 17, 1949

VERY and Ellis<sup>1</sup> and Avery and Morrison<sup>2</sup> have shown that for certain hydrocarbons many of the infra-red absorption bands are very considerably narrowed when the temperature is reduced. The above authors give conclusive evidence that Bjerrum's formula is valid even in the liquid and solid state for the particular cases which they have investigated.

Walsh and Willis<sup>3</sup> have recently questioned the phenomenon of temperature narrowing of infra-red bands in a single phase (liquid or solid) attributing the effect to change in phase. Study of the papers of Avery and Ellis<sup>1</sup> and Avery and Morrison<sup>2</sup> does not support the contention of Walsh and Willis.<sup>3</sup> Comparison of the low temperature spectrum of Avery and Ellis with A.P.I. Spectrogram No. 245 for liquid 2, 2 dimethylbutane is completely unjustified since comparison of line breadth is impossible due to widely different instrumental factors entering into the two above mentioned spectra.

We have recently investigated<sup>4</sup> the infra-red absorption spectra of a number of hydrocarbons at different temperatures through much of the liquid and solid range. Our investigation was concerned chiefly with the occurrence of rotational isomers and not in a discussion of band breadth. However, in the case of all the spectra which we have investigated, one of the most prominent features was the distinct sharpening of the bands as the temperature was reduced.

Reduction of band width with decreasing temperature in the liquid phase was immediately apparent since in many cases double bands were merely resolved as shoulders at room temperature while at low temperature clean resolution of these doublets was achieved. In addition, the narrowing of the bands was considerably greater than mere appearance of the curves would indicate. (Since the cell thickness is sensibly constant and the density of the liquid increases with decrease of temperature, more molecules are in the absorbing beam at low temperature than at high temperatures. The effect of increased absorbing path would be to decrease the transmission and make the bands appear wider from this cause alone. For quantitative measurements it is of course necessary to compare band widths at the same percentage transmission as Avery and Ellis<sup>1</sup> have done.)

The curves shown in our paper,<sup>4</sup> Figs. 1 to 5, for *n*-pentane, *n*-hexane, *n*-heptane, 2 methylbutane and 2:3 dimethylbutane are reproduced on too small a scale to show clearly the large effect of temperature on narrowing of these absorption bands.

We wish to point out further that the narrowing of Raman lines at low temperatures in liquids can be easily and unequivocally observed for a number of the hydrocarbons. Microphotometer curves of the Raman spectrum of liquid *n*-butane at 300°K and 147°K obtained by one of us<sup>5</sup> clearly show the effect of temperature in narrowing these bands.

We are not aware of any incontrovertible evidence in the literature where distinct rotational fine structure has been found in the infra-red absorption spectrum of a liquid. The situation with respect to solids is similar.<sup>6</sup> In spite of the lack of direct spectroscopic evidence for the existence of discrete rotational and rotational vibrational states in a liquid, the breadth and temperature behavior of many infra-red bands yields indirect spectroscopic evidence for rotation. It seems plausible that discrete rotational structure is not to be expected in a liquid since the pressure broadening of the lines would be extremely large.

The observation of Avery and his co-workers<sup>1,2</sup> that quantitatively certain infra-red bands in liquids and solids follow Bjerrum's formula with regard to their breadth as a function of temperature can only be considered to be fortuitous in its strict quantitative aspect. It is certain that at the present time our

knowledge of the liquid state is insufficient to give a strictly quantitative theoretical treatment to this problem, but it should be expected that the behavior of gases should furnish a first crude approximation.

Finally we wish to emphasize the point that many of the infrared absorption bands in a liquid (for small hydrocarbon molecules) sharpen very markedly as the temperature is decreased. A similar phenomenon can also be observed with regard to some Raman lines of certain liquids.

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### Carrier-Free Radioisotopes from Cyclotron Targets. III. Preparation and Isolation of $\text{Sb}^{122, 124}$ from Tin\*

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DEUTERON bombardment of tin produces<sup>1</sup>  $\text{Sb}^{122, 124}$  by the nuclear reactions  $\text{Sn}^{122}(d, 2n)\text{Sb}^{122}$ ,  $\text{Sn}^{124}(d, 2n)\text{Sb}^{124}$ . The present paper reports a carrier-free method of isolating these activities from the target element and from the radioisotopes of indium ( $n, p$ ) and cadmium ( $n, \alpha$ ) which are formed concurrently by secondary neutrons produced by the 19 Mev deuteron beam of the 60-inch medical cyclotron at Crocker Laboratory. Other possible<sup>2</sup> shorter-lived radioisotopes of antimony were allowed to decay out prior to the chemical separation.

The target was a block of C.P. tin, soft soldered to a water-cooled copper plate. It was bombarded with 19 Mev deuterons for a total of 83.1  $\mu\text{a}$ -hr. in the 60-inch cyclotron at Crocker Laboratory. The bombarded surface was removed by milling.

0.5 gram of turnings were dissolved in a minimum volume of aqua regia. 12 N HCl was added to destroy excess  $\text{HNO}_3$  and the solution was diluted to approximately 25 ml of 0.1 N HCl. 10 mg of cadmium were added and precipitated with  $\text{H}_2\text{S}$  after addition of 1 g of oxalic acid to prevent<sup>3</sup> precipitation of tin sulfide. The antimony activity carried quantitatively. The CdS was dissolved in HCl plus oxalic acid, reprecipitated with  $\text{H}_2\text{S}$ , dissolved in a minimum volume of 12 N HCl and transferred to an all-glass distilling flask.<sup>4</sup> 16 ml of 60 percent  $\text{HClO}_4$  were added and traces of tin were distilled<sup>5</sup> at 200°C during the gradual addition of 10 ml of 12 N HCl. Approximately 98 percent of the carrier-free antimony remained in the residue. The antimony activity was then distilled with the gradual addition of 10 ml of 40 percent HBr. The distillate contained 95 percent of the  $\text{Sb}^{122, 124}$ . Indium and cadmium were retained in the residue.

To obtain carrier-free radio-antimony in isotonic saline for subsequent biological investigation, the distillate was treated with aqua regia to destroy HBr and evaporated to dryness on 40 mg of NaCl. The activity dissolved quantitatively with the addition of 5 ml of distilled water.

The decay curve was followed for 300 days and showed two periods: 2.8-day  $\text{Sb}^{122}$  and 60-day  $\text{Sb}^{124}$ . One month after bombardment, the activity contained only 60-day  $\text{Sb}^{124}$ ; mass absorption measurements in Pb showed the 1.7 Mev gamma-ray previously reported.<sup>3</sup> A tracer amount of carrier-free antimony was added to a solution containing milligram amounts of tin, antimony and indium; the antimony fraction was separated chemically<sup>6</sup> and contained 98 percent of the activity.

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### Carrier-Free Radioisotopes from Cyclotron Targets. IV. Preparation and Isolation of $\text{Mn}^{54}$ and $\text{Co}^{56, 57, 58}$ \*

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CARRIER-FREE radioisotopes of manganese and cobalt of useful half-life may be obtained only by cyclotron bombardment. The present paper describes chemical methods of isolating  $\text{Mn}^{54}$  and  $\text{Co}^{56, 57, 58}$  from an iron target bombarded with 19-Mev deuterons in the 60-in. cyclotron at the Crocker Laboratory. At this energy,  $\text{Mn}^{54}$  and  $\text{Co}^{56, 57, 58}$  are produced in a thick target by the nuclear reactions:<sup>1</sup>  $\text{Fe}^{56}(d, \alpha)\text{Mn}^{54}$ ,  $\text{Fe}^{56}(d, 2n)\text{Co}^{56}$ ,  $\text{Fe}^{56}(d, n)\text{Co}^{57}$ ,  $\text{Fe}^{57}(d, 2n)\text{Co}^{57}$ ,  $\text{Fe}^{57}(d, n)\text{Co}^{58}$ . Other possible shorter-lived radioisotopes of manganese and cobalt were allowed to decay out prior to the separation.

The iron<sup>2</sup> target was silver-soldered to a water-cooled copper probe and bombarded for 2000  $\mu\text{a}$ -hr. at an average beam intensity of approximately 50  $\mu\text{a}$ . The bombarded surface was dissolved off in 6N HCl.

All but approximately 10 mg of the target iron was extracted with ether. The aqueous phase was neutralized with  $\text{NH}_4\text{OH}$ , a few drops of bromine were added, and  $\text{Fe}(\text{OH})_3$  was precipitated with 15N  $\text{NH}_4\text{OH}$  in excess. Under these conditions carrier-free radio-manganese was quantitatively carried, presumably in the quadri-valent state. Over 98 percent of the radio-cobalt remained in the supernatant.<sup>3</sup> The  $\text{Fe}(\text{OH})_3$  plus radio-manganese was reprecipitated twice with  $\text{Br}_2\text{—NH}_4\text{OH}$  in the presence of 1 mg of cobalt hold-back carrier. Three additional precipitations removed traces of carrier cobalt. The  $\text{Fe}(\text{OH})_3$  was washed, dissolved in 6N HCl and iron was extracted with ether. The solution of carrier-free radio-manganese in 6N HCl was evaporated to dryness after the addition of 5 ml of isotonic saline solution. Addition of 5 ml of distilled water gave an isotonic solution of carrier-free  $\text{Mn}^{54}$  for subsequent biological experiments.

The activity was identified by the 310-day half-life and by the 0.85-Mev gamma-ray reported<sup>4</sup> for  $\text{Mn}^{54}$ . As further identification, a small amount of activity added to a solution containing carrier amounts of Mn, Fe, and Co was quantitatively recovered in the Mn fraction from a chemical separation.<sup>5</sup>

The supernatant from the first  $\text{Fe}(\text{OH})_3$  precipitation containing carrier-free radio-cobalt,  $\text{NH}_4\text{Cl}$ , and  $\text{NH}_4\text{OH}$  was evaporated to dryness and treated with 16N  $\text{HNO}_3$  to destroy ammonium salts. 12N HCl was added to remove  $\text{HNO}_3$  and the solution was evaporated to dryness on 40 mg of NaCl. The activity dissolved quantitatively in 5 ml of water.

The radio-cobalt showed the 72-day half-life of  $\text{Co}^{56, 58}$ ; after 200 days the longer period of  $\text{Co}^{57}$  was apparent. In addition, chemical separation with added Mn, Fe, and Co carriers identified the activity as cobalt. Mass absorption measurements showed the 1.2-Mev beta-reported<sup>6</sup> for  $\text{Co}^{56}$ . The combined gamma-radiation had a half-thickness of approximately 10 g/cm<sup>2</sup> in lead.