Heat-Pipe Oven for Homogeneous Mixtures of Saturated and Unsaturated Vapors; Application to NaLi

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A heat-pipe oven has been developed to produce homogeneous mixtures of a saturated vapor with an unsaturated vapor at any arbitrary well-defined ratio. The oven is able to handle materials of widely different vapor pressures and the zone containing the homogeneous vapor mixture can be made to extend over any desired path length. With this heat-pipe oven containing sodium and lithium, the laser- and collision-induced fluorescence spectrum of the NaLi molecule has been used to study the operation of the oven. The first observation of a "propensity rule" for a polar molecule (the $\Delta J = +1$ collision-induced NaLi line is stronger than the corresponding $\Delta J = -1$ or 0 line) is reported.

I. INTRODUCTION

In microwave or spectroscopic absorption experiments of molecular vapors it is desirable to have large path lengths of these vapors at low total pressures to prevent pressure shift or broadening effects. There has been no simple technique until now for producing arbitrary mixtures of vapors of materials that have widely different vapor pressure curves and fit the above requirements. We have developed a heat-pipe oven that is able to generate long path lengths of mixtures of saturated and unsaturated vapors in arbitrary well-determined ratios and total pressure. This device is based on a modification of a concentric heat-pipe oven recently developed by Vidal and Haller (henceforth referred to as paper I) which produces well-defined mixtures of pure metal vapors and inert gases.

Sodium and lithium are the materials used in our heat-pipe oven. We are able to study the operation of this oven by means of laser-induced resonance fluorescence of the Na, Li, and NaLi molecules formed within the oven.

Hessel and Jankowski studied the operation of an ordinary heat-pipe oven when it contained two different materials. They found that the two materials may under certain conditions form separate zones within the pipe, and that the vapors mix in the transition area between the zones. They used a heat-pipe in the shape of a cross to move the interface between the zones to the crossing point, and observed the spectra of the NaLi molecule for the first time by means of laser-induced resonance fluorescence. In their oven the interface or mixing region extended over only a few centimeters path length and the vapor density of Na and Li in the mixing region was inhomogeneous and could not be easily determined. We will show in this paper that the operation of their heat-pipe corresponds to a special case of our modified concentric heat-pipe, and that we are able to obtain mixing of the two vapors over any arbitrary length of the pipe with the density of the component vapors uniform and determined in a simple manner.

II. PRINCIPLE OF THE CONCENTRIC HEAT-PIPE OVEN FOR VAPOR MIXTURES

In the following discussion we will explore the ways to obtain from two materials A and B a homogeneous mixture of their vapors at some arbitrary well-defined ratio. In Fig. 1 two vapor pressure curves are shown—the vapor pressure curves of lithium (material A) and sodium (material B). These materials were used in the experiments described in this paper. If one puts both substances into a container, the ratio of the partial pressures is given by the vapor pressure curves at the temperature of the coldest point of the system, as long as the vapors are saturated (viz., they are in equilibrium with their liquid phase). At some temperature $T_s$, the ratio of the partial pressures is $P_A/P_B$. The ratio of two particular saturated vapors is therefore completely specified by the temperature. In order to obtain ratios different from this fixed ratio, one would have to reduce the amount of material available until at least one of the vapors is no longer saturated. In practice, it is very difficult to maintain a stable situation with a well-defined ratio by this method over long periods of time. Any change in temperature or chemical reaction of the material with the container would alter the ratio.

We now describe a modification of the concentric heat-pipe oven, which is capable of generating homogeneous mixtures of a saturated and an unsaturated vapor at a well-defined and an easily adjustable arbitrary ratio. Its schematic arrangement is shown in Fig. 2. Like the concentric heat-pipe oven described in paper I it consists of an inner, open-ended heat pipe which is concentrically surrounded by another open-ended heat pipe of larger diameter. The outer heat pipe is heated by means of an induction heater. The inner side of the outer pipe and the outer and inner side of the inner pipe are covered by a mesh structure acting as a wick. The crucial difference with respect to the concentric heat-pipe oven in paper I is the fact that over a length $L$ the wick is removed in the center section of the inner wick of the inner pipe. The significance of this becomes clear from the following discussion.

While the outer heat pipe is filled with a substance A (in our case lithium), the inner pipe contains both materials A and B (lithium and sodium). The pressure of the
confining inert gas is $P_s$ in the outer pipe and $P_a$ in the inner pipe, with $P_a$ always greater than $P_s$. By heating the outer heat pipe at a power level where it acts like an ordinary heat-pipe oven, the outer heat pipe serves as the ideal heater described in paper I. For a particular vapor pressure curve, its temperature $T_e$ is completely specified by the confining inert gas pressure $P_s$. It is important to remember that in order to prevent hot spots, the outer wick of the inner pipe and the inner wick of the outer pipe have to be connected by a wick structure in order to avoid depletion of material on the inner wick of the outer pipe. This problem was avoided by a loop-shaped wick shown in Fig. 1 of paper I.

In order to understand the behavior of the inner heat pipe, we must realize that it contains two materials with different vapor pressure curves. In an ordinary heat-pipe oven the temperature-pressure characteristic is determined by the vapor pressure curve of the substance with the larger vapor pressure. In the case of the inner heat pipe in Fig. 2, we have to distinguish between the center section $L$, without a wick on the inner side, and the two adjacent sections which have a wick on the inner side.

When the center section of the outer pipe containing pure $A$ (lithium) is heated, the confining gas pressure $P_s$ forces the center section of both the inner and outer pipe to have a temperature $T_a$. Since initially both materials $A$ and $B$ are in the central section $L$ of the inner pipe, the partial pressure in the inner pipe of $A$ (lithium) is $P_a$ and of $B$ (sodium) is $P_{eB}$, as indicated in Fig. 1, as long as both vapors are saturated.

If however, the inner pipe confining inert gas pressure $P_s$ is less than $P_a$ but greater than $P_{eB}$, the vapor of substance $B$ is driven out to the cooler areas of the pipe, while substance $A$ remains in equilibrium with its liquid phase. Since there is no wick in the center section, the $B$ (sodium) liquid vaporizes and becomes depleted since it cannot return. $B$ (sodium) is now unsaturated in the center section $L$, and has a partial pressure $P_{eB} - P_a$. In this manner we have achieved in the inner pipe center section an unsaturated vapor $B$ (sodium) of partial pressure $P_{eB} - P_a$ and a saturated vapor $A$ (lithium) with pressure $P_a$. The partial pressures are completely specified by the inert gas pressure $P_s$ of the outer pipe and $P_a$ of the inner pipe.

Without the wick on the inner side of the inner pipe, both substances would be deposited at the cooling chambers on both ends of the inner pipe, after some time of operation. To avoid this, both materials are returned by capillary action of the two wick-covered sections adjacent to the center section $L$. Both materials $A$ and $B$ are present in their liquid phase in the wick-covered sections of the inner pipe. Hence we have an outer heat pipe operated with substance $A$ (lithium) and an inner heat pipe whose properties are dominated by substance $B$ (sodium) since the vapor pressure is greater than that of substance $A$. From the vapor pressure curves in Fig. 1 we realize that the outer heat pipe with a confining pressure $P_s$ wants to operate at temperature $T_e$, while the inner heat pipe with a confining pressure $P_a$ wants to operate at temperature $T_a$. The result is that the inner heat pipe cools the outer heat pipe very heavily, such that for the outer heat pipe the length of the zone at temperature $T_e$ is just as long as the length $L$ of the center section of the inner pipe without a wick. One finally obtains a stable equilibrium such that the power fed into the outer heat pipe is balanced by the power radiated and conducted from the outer pipe surface as well as by the power removed by the inner pipe. The power removed by the inner pipe is in turn radiated to the surrounding cooler portion of the outer pipe, and if this heat sink is not large enough, the cooling chambers remove the rest by conduction.

If the power balance is not carefully adjusted, there are some important practical consequences. First of all, we find that the input power of the heating element should not exceed the power required to maintain a heated section of length $L$ at the temperature $T_e$. If one significantly surpasses this optimum power level, most of the excess power is removed through the inner pipe by the cooling chambers. As a result, the material $B$...
with the larger vapor pressure is eventually completely condensed at the cooling chambers, as we have observed experimentally. By reducing the input power, one shortens the length of the heated zone of temperature $T_u$. Hence one also reduces in the inner pipe the length of the section over which the saturated and unsaturated vapors are mixed.

The behavior of the inner heat pipe is summarized in Fig. 3, which shows schematically the distribution of the temperature and the various partial pressures along the inside of the inner heat pipe for the maximum desirable input power explained above. The center section, whose length $L$ has no wick, has a temperature $T_u$ that is determined by the confining pressure $P_s$ of the outer pipe. The partial pressure of saturated vapor of the substance $A$ (lithium) is therefore $P_s$, while the partial pressure of the unsaturated vapor of the substance $B$ (sodium) is $P_s - P_s$. Outside the center region the temperature drops and its value $T_u$ is determined by the vapor pressure curve of substance $B$ at the confining pressure $P_s$. Consequently, the partial pressure of substance $A$ essentially vanishes, while the partial pressure of substance $B$ rises to $P_s$. The length of the vapor zone at temperature $T_u$ is determined by the input power. Outside this range, material $B$ condenses and the partial pressure of substance $B$ vanishes, so that the confining inert gas pressure rises up to $P_s$. As in other heat-pipe ovens, the inert gas prevents any possible chemical reactions of the vapor with the optical window.

For the special case in which the confining inert gas pressures of the inner and outer heat pipes are identical, $P_s = P_s$, it is clear that the partial pressure of substance $B$ vanishes in the center section without a wick. One therefore obtains a center zone which contains only the saturated vapor of substance $A$ (lithium), confined by two adjacent zones containing the saturated vapor of substance $B$ (sodium). This mode of operation corresponds exactly to the two-metal heat-pipe oven described by Hessel and Jankowski. It does not give homogeneous mixtures of two different vapors. Only in the transition range one obtains mixtures of the two vapors whose partial pressures and temperature change rapidly as a function of position.

We also note that by raising the confining inert gas pressure $P_s$ of the inner pipe above the value $P_s$ in Fig. 1, the concentric heat pipe in this paper operates like the concentric heat pipe in paper I. In this mode it does not matter any more whether the center section of the inner pipe is covered by a wick or not, since both vapors are then in equilibrium with their liquid phase. Note that we now uniformly mix the homogeneously mixed vapor with the inert gas over the heated length which may now be even longer than the wickless center section $L$. We have at some temperature $T_u$ in the inner pipe a partial pressure $P_s$ of saturated vapor of substance $A$, a partial pressure $P_s$ of saturated vapor of substance $B$, and a partial pressure of the inert gas ($P_s - P_s - P_s$).

### III. SPECTROSCOPIC INVESTIGATIONS OF THE NEW HEAT-PIPE OVEN

Our first concentric heat-pipe oven that handles mixtures of two different vapors was built out of stainless steel and operated with sodium and lithium. Details of the pipe are described in paper I. To study the operation of the pipe, we investigated the resonance fluorescence spectra of the NaLi, Na$_2$, and Li$_2$ molecules. For this purpose, light from an argon-ion laser was passed into the back end of the heat pipe and the resonance fluorescence radiation exiting from the front end was focused into the slit of a 2-m-grating spectrometer.

By means of the 4965-Å line of the argon-ion laser we first observed the NaLi resonance fluorescence spectrum which will be discussed in more detail in Sec. IV. At a pressure $P_s = 1$ Torr (1.33×10$^4$ N/m$^2$) and $P_s = 2$ Torr, one has a 1:1 mixture of sodium and lithium with both partial pressures being equal to 1 Torr. In this case the resonance fluorescence spectrum of NaLi was more intense than that of Na$_2$ and Li$_2$. It should be emphasized that for the spectroscopic observation of the NaLi molecule it is crucial to have a system in which both constituents have similar abundances. In a system in which both vapors are saturated, the ratio of the partial pressures for sodium and lithium is close to 200, and the resonance fluorescence spectrum of NaLi is completely obscured by that of Na$_2$.

We were able to observe the $v''$ progression of the NaLi resonance fluorescence series ($v'' = 28$) up to $v'' = 10$, where $v''$ is the lower-state vibrational quantum number. At partial pressures of the constituents around 1 Torr, the most intense member in the series is the one with $v'' = 6$, for which Fig. 4 shows a photoelectric scan. Lowering the partial pressures to 0.1 and 0.03 Torr, the relative intensity of the first members in the progression increases noticeably. This is in agreement with the observations of Hessel$^4$ who found the first two members in the series to be the most intense ones. It indicates that the first members are strongly self-absorbed at higher pressures. It also supports the fact that the sodium-lithium mixture exists over an extended zone as compared to the short transition zone of Hessel and Jankowski.$^3$
As a further test of the behavior of the concentric heat-pipe oven, we connected the outer and inner pipe such that $P_0 = P_1$. In this case, as explained above, a center zone of pure saturated lithium vapor is confined by two pure saturated sodium zones. This was clearly demonstrated by means of a He-Ne laser which generates strong resonance fluorescence with the $\text{Na}_2$ molecule and very little fluorescence with the $\text{Li}_2$ molecule. The small intensity of the latter fluorescence was also tested independently in a pure lithium heat-pipe oven. Hence one observes a strong red fluorescence in both confining sodium vapor zones and a very faint fluorescence in the center area.

IV. RESONANCE FLUORESCENCE SPECTRA OF THE $\text{NaLi}$ MOLECULE

In this section we give a more detailed report concerning the laser-induced resonance fluorescence spectra of the $\text{NaLi}$, $\text{Na}_2$, and $\text{Li}_2$ molecules.

In all three cases we observed the $^1 \Sigma - ^3 \Pi$ system of the molecules. All transitions obey the rotational selection rules $\Delta J = 0, \pm 1$ and the selection rules for electric dipole radiation which permit only transitions between levels of opposite parity. The additional symmetry selection rule for homonuclear molecules, that symmetric levels can only combine with symmetric levels and antisymmetric with antisymmetric, does not lead to new restrictions for our case of interest.

In the laser-induced resonance fluorescence spectra, the laser line may either excite the upper level ($c$ level) or the lower level ($d$ level) of the $\Lambda$-type doublets in the upper electronic $^3 \Sigma$ state. Consequently, as explained in detail for the $\text{Na}_2$ molecule and the $\text{Li}_2$ molecule, one obtains in the first case a $v''$ progression of $P$ and $R$ lines, and in the second case a $v''$ progression of $Q$ lines.

Besides these "parent lines" one obtains weaker "satellite lines" which are due to transitions from neighboring rotational vibrational levels populated by inelastic collisions from the laser-populated level. Depending on whether one is dealing with a homonuclear molecule like $^2 \text{Na}_2$, $^2 \text{Li}_2$, $^2 \text{Li}_4$ or with a heteronuclear molecule like $\text{NaLi}$ or $^4 \text{Li}^7 \text{Li}$, one has different patterns for the satellite lines. For a homonuclear molecule with zero nuclear spin one has the perfectly rigorous selection rule that in an inelastic collisional transition the molecular symmetry has to be preserved. If the nuclear spin differs from zero this selection rule is still very strong owing to the weak coupling of the nuclear spin with the rest of the molecule as shown for $\text{Na}_2$, $^7 \text{Li}_2$, $^7 \text{Li}_4$ and with a heteronuclear molecule like $\text{NaLi}$ or $^6 \text{Li}^7 \text{Li}$, one has different patterns for the satellite lines. For a homonuclear molecule with zero nuclear spin one has the perfectly rigorous selection rule that in an inelastic collisional transition the molecular symmetry has to be preserved.

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In case of a heteronuclear molecule, the symmetry selection rule for inelastic collisional transitions has almost completely lost its meaning and as a result one always obtains the even $P$, $Q$, and $R$ satellite lines if the laser excites a state of positive parity. In case of a heteronuclear molecule, the symmetry selection rule for inelastic collisional transitions has almost completely lost its meaning and as a result one always obtains the even $P$, $Q$, and $R$ satellite lines if the laser excites a state of positive parity.
Intensity alteration with those lines which are forbidden for a homonuclear molecule, being weaker as observed already for the $^7\text{Li}^-^7\text{Li}$ molecule, and shown below for the NaLi molecule.

In the concentric heat-pipe oven designed to handle mixtures of sodium and lithium, we observed the resonance fluorescence spectrum of the NaLi molecule excited by the 4965-Å line of the argon-ion laser. This spectrum was first observed by Hesse in a crossed two-metal heat-pipe oven outlined in Sec. I. Figure 4 shows a photoelectric scan of one member in the $^2\Sigma^+$ progression with $v'' = 6$ of the laser-induced $P$ and $R$ series of the NaLi molecule. In Fig. 4 the $P$ and $R$ parent lines, originating from the laser-populated rotational-vibrational level in the $^1\Pi$ state of the NaLi molecule, are off scale by about a factor of 10. The photoelectric scan of the spectrum reveals very clearly the satellite lines which originate from neighboring rotational-vibrational levels populated by inelastic collisions. The corresponding change in angular momentum $\Delta J$ is indicated below the spectrum. Transitions with $\Delta J < 10$ have been observed and the spectrum is hardly affected at all by the few weak Na$_3$ fluorescence lines. The intensity alteration of the satellite lines explained above for a heteronuclear molecule is most clearly visible for the $Q(28)$ line ($\Delta J = 0$), which stems from a collisional transition to the other $\Lambda$-type doublet level with the same $J'$. The intensity alteration disappears completely for large $\Delta J$. It is interesting to note that a more pronounced intensity alteration was observed for the $^7\text{Li}^-^7\text{Li}$ molecule. In our case the $Q(27)$ line ($\Delta J = -1$) is more intense than the $Q(29)$ line ($\Delta J = +1$). The origin of this propensity rule is not yet understood.

V. CONCLUSIONS

We have demonstrated that the concentric heat-pipe oven can be modified so as to produce large concentrations of molecules like NaLi over an extended path length. This arrangement considerably enhances the possibilities for microwave or optical-absorption studies of these molecules. In addition, quantitative collisional studies of such polar molecules can be made either in the vapor of the constituent atoms or mixed in a vapor with an inert gas.

One should operate this concentric oven at the optimum power level so that the mixed-vapor path length is maximized and the confining vapor zone is minimized.

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4M.M. Hessel, Phys. Rev. Letters 26, 215 (1971). The experiment has been repeated by M. Hessel using a $^7\text{Li}$ isotope of 99.99% purity. This leaves no doubt that the resonance fluorescence spectrum observed is due to the NaLi molecule.