13 January 1967, Volume 155, Number 3759 **SCIENCE**

# Stellar and Other High-Temperature Molecules

"Hot" molecules can be investigated spectroscopically when trapped at 4 degrees Kelvin.

William Weltner, Jr.

Some molecules are observed only under high-temperature conditions, as in the atmospheres of stars, in arcs, or in the vapor over very refractory solids. Spectroscopic studies of such sources are usually difficult because the molecules are thermally excited into many rotational and vibrational levels which broaden the bands and multiply their number. Even if the analysis problems are solved, the ground electronic state may not be unambiguously determined because of other low-lying states populated at the high temperatures.

And so one may ask the almost rhetorical question, Can these molecules be observed at a lower temperature? The answer is usually "no" if the experiments are limited to the study of gases, but it is "yes" if the molecules are observed after being trapped in an inert, transparent solid. The investigation of molecules in such an environment can provide valuable information in spite of the influence of the surrounding medium, and such a technique is proving to be very helpful in clarifying the properties of high-temperature molecules.

## High-Temperature Molecules

In general, stars in the same class as the sun and all cooler stars exhibit the spectra of molecules in their atmospheres (*1*). The disk of the sun, a class G star, is really too hot (~ 6000°K) for many molecules to exist there, but the sun's proximity to us makes up for the low population and weak molecular spectra. The sunspots are at a lower temperature, and observation of those regions leads to the definite identification of 11 molecules, as indicated in Table 1. Others are known to be present, but there is doubt as to their identity.

The cool red stars of classes M, S, R, and N have surface temperatures of less than 3000°K, and molecules are more abundant in their atmospheres. It is also well known that the molecules which dominate the spectra of red stars vary with the ratio of oxygen to carbon in their atmospheres. Class M stars are characterized by a strong TiO spectrum; class S stars, by strong ZrO bands; class R and class N stars, by $C_2$ and CN bands. The latter are usually called class C or "carbon" stars. Almost all of the stellar molecules listed in Table 1 are simple diatomic species; $C_3$, $SiC_2$, and $H_2O$ are the only polyatomic molecules definitely known to be present, although there is reason to believe that polyatomic species may actually predominate in some cases (*2*).

In studies of the atmospheres of these stars there is increasing recognition of the role played by the molecules in the absorption of light from the inner regions (photosphere) of the stars. Such "blanketing" effects can distort the emitted radiation markedly in certain wavelength regions when molecules such as TiO or $C_3$ are present in relatively high concentrations.

Other molecules, not found in stars, exist at the same high temperatures but derive their importance from modern technology. Because of their high melting points, the refractory metals (such as tantalum, molybdenum, tungsten), oxides, and carbides are vital to the rocket and space industries. In recent years, mass spectrometry has played an increasingly important role in determining the molecular species vaporizing from such refractories at high temperatures, since it also allows determination of the thermodynamics of the process and the dissociation energies of the molecules (*3*). Ultimately, however, for thermodynamic or other reasons, one is again faced with a need to know the more intimate properties of these "hot" molecules, and observing them trapped in a solid at 4°K has helped provide that information.

## Matrix-Isolation

Matrix-isolation is a technique for trapping molecules as isolated entities in an inert solid, or matrix, in order to investigate their properties, usually by optical means. It has been largely developed by G. C. Pimentel, G. W. Robinson, and their co-workers, and by A. M. Bass and H. P. Broida and the members of the now disbanded Free Radicals Research Program at the National Bureau of Standards (*4*). My principal concern, here, is to make clear the advantages, disadvantages, and results of the application of this technique to the study of "hot" molecules; however, much of what is said concerning the effects of matrices upon the trapped molecules applies to all matrix work.

In most spectroscopic studies of stellar molecules in the laboratory the molecules are produced in an arc be-

---

The author is now professor of chemistry at the University of Florida, Gainesville. This review is based upon work done at the Union Carbide Research Institute, Tarrytown, New York.

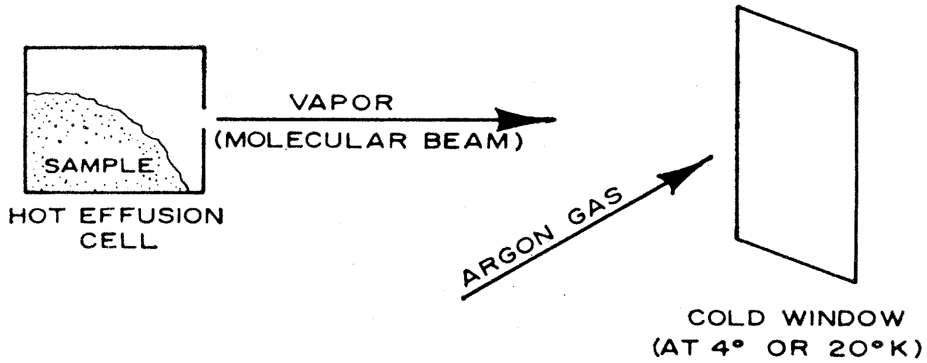

Fig. 1. Matrix-isolation technique as applied to molecules vaporizing at a high temperature. (There are approximately 1000 molecules of argon per molecule of sample vapor.)

tween electrodes fabricated from the metallic elements, or between carbon electrodes containing a powder or solution to produce the desired species. However, the source used in matrix isolation is usually a Knudsen cell, from which the effusing vapor is trapped in the manner shown schematically in Fig. 1 (*5*). Such a cell has been used in numerous investigations of the mass spectra of vapors in equilibrium with refractory solids, made over the last 10 years by Inghram, Chupka, Berkowitz, and many others (*3*). Because of the existence of data from such studies on the composition of these vapors, it is expedient to use the same source in matrix isolation. One then knows just what kinds of molecules are issuing from the effusion cell, and almost always a suitable sample can be found for producing the desired stellar molecule, perhaps mixed with other molecules. For example, carbon vaporizes at about 2500°K, to C, $C_2$, and $C_3$ (*6*), and $C_3$ has been studied while trapped in a matrix at liquid helium temperatures (4°K). Moreover, ZrO and TiO can be obtained through vaporization of the solid oxides or by passing oxygen into a tungsten cell containing zirconium or titanium metal (*7, 8*). Often it is also necessary to observe isotopically substituted molecules, and these can be prepared by passing an isotopically labeled gas, such as $^{18}O_2$, into the Knudsen cell containing the metal, or by vaporizing the separately prepared solid.

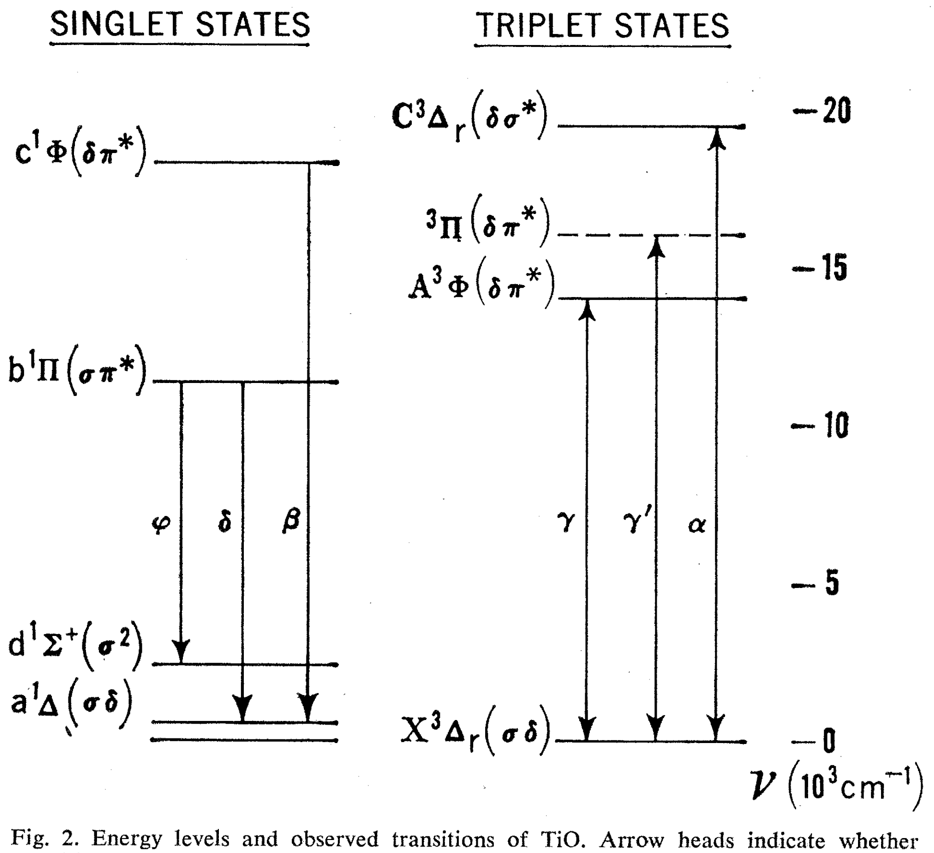

Fig. 2. Energy levels and observed transitions of TiO. Arrow heads indicate whether transitions were observed in emission or in absorption or in both. [From *8*, reproduced by permission of the *Journal of Physical Chemistry*]

The matrix material can be any gas which will not react with the trapped molecule and which can be conveniently and rigidly solidified. The rare gases are usually used because they are relatively inert and offer a wide range of melting points and atomic sizes. Neon can be used only with liquid helium as the refrigerant, since it melts at 24°K and diffusion in the solid state probably begins at about 12°K. Argon, krypton, and xenon can all be used with liquid hydrogen (boiling point, 20°K) as the refrigerant. The choice of matrix gas is determined partially by these factors but, more importantly, by the effect the solid matrix will have upon the trapped molecule. The objective in matrix isolation is, of course, to trap the molecules in a condition which is as much like the gas condition as possible. As one would expect, the matrix composed of the least-polarizable atoms perturbs the trapped molecule least, thus neon is usually found to be the best matrix gas.

## Optical Spectroscopy

The advantage of making spectroscopic measurements on a molecule at 4°K lies in the fact that, at that temperature, the molecule is in its lowest energy state and vibrational or electronic transitions induced by light always begin from that level. Although this simplifies the absorption spectrum, holding the molecule in a solid in order to study it at 4°K does cause, as mentioned above, some alteration in its properties.

In order to observe the degree of alteration in the spectrum of a gas molecule when it is trapped in a matrix, let us take TiO as an example (*8*). In Fig. 2 the electronic energy levels of TiO are shown, together with the transitions observed in gas emission spectra (downward pointed arrows) and in matrix absorption spectra (upward pointed arrows). The ground state is $^3\Delta_r$, and

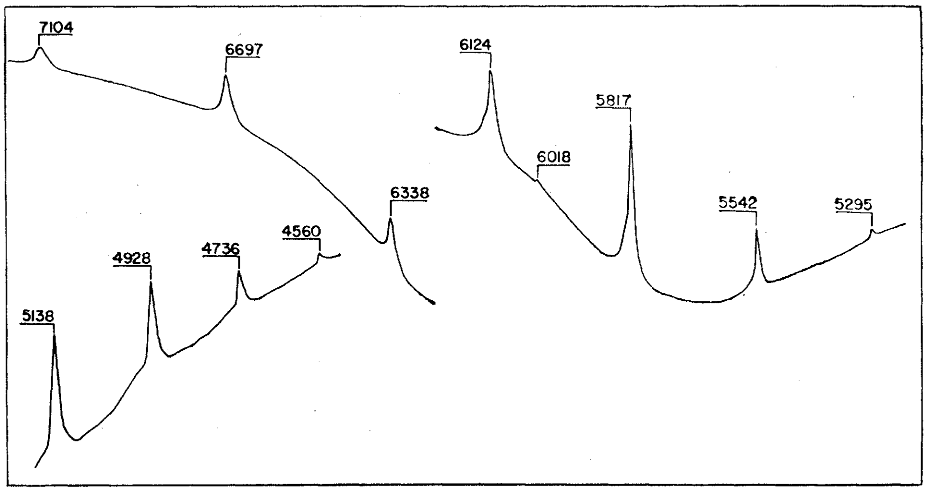

Fig. 3. Absorption spectrum of $Ti^{16}O$ in a neon matrix at 4°K. Wavelengths are in angstroms. [From *8*, reproduced by permission of the *Journal of Physical Chemistry*]

since all molecules at 4°K are in the lowest energy state in the matrix (that is, $^3\Delta_1$ in this case), absorption is observed to occur only from that level to the A $^3\Phi$, $^3\Pi$, and C $^3\Delta$ upper levels. These band systems have been designated $\gamma$, $\gamma'$, and $\alpha$ by the spectroscopists who first studied them (*9*). The matrix spectrum is shown in Fig. 3. Table 2 gives a comparison of the positions of the (0,0) bands of each of these systems in the gas and in neon and argon matrices. Also given is the vibrational frequency in the excited electronic state as deduced from the band structure in the gas and in neon and argon matrices. Note that the gas and neon-matrix values are in the closest agreement; the excited electronic levels lie farther above the ground state in neon than in the gas (by about 100 waves per centimeter), and the vibrational frequencies differ by no more than 5 $cm^{-1}$. The vibrational frequency in the ground $^3\Delta_1$ state (not shown in Table 2) was found to be 1005 $cm^{-1}$ in neon at 4°K, as compared to 999.2 in the gas (*8, 10*). This is the kind of correspondence which one can generally expect to find between gas and neon-matrix data.

I have made no mention of rotational structure in matrix spectra because, in general, the trapped molecules do not rotate. The molecules $H_2O$, HCl, $NH_3$, and $NH_2$ do have interesting rotational (and translational) motion in matrices (*11*), but consideration of such motion here is not essential to the discussion. Usually all of the valuable information obtained from analysis of such structure in the gas phase—that is, information on types of electronic transitions and interatomic distances—is lost in matrix spectra.

The shapes and widths of bands vary greatly in matrices, depending upon the extent of the interaction between the trapped molecule and the solid. In the case of TiO, discussed above, the bands corresponding to electronic-vibrational transitions have a width of about 15 $cm^{-1}$ (at half height) in neon matrices at 4°K. This is also the case for VO (*12*), ZrO, HfO (*8*), and TaO (*13*). The band widths of these molecules in argon are considerably greater, lying in the range of 150 to 220 $cm^{-1}$. This greater width is particularly detrimental if bands are close together, as in TaO (*13*), since individual bands are obscured and analysis is difficult. The bands may be broad even in neon. This occurs, for example, in $SiC_2$ matrices (*14*), where, however, the characteristic shape of the bands makes analysis easier.

In matrix absorption spectra the bands in a particular progression (transitions from vibrational level $v'' = 0$ in the ground state to $v' = 0, 1, 2, \ldots$ in an excited state) always have the same shape, a fact which is helpful for identification. (Note that here matrix perturbations are beneficial.) Generally the departure of the shape from the usual Lorentzian form is determined by one or both of two factors: (i) the occupation of multiple sites in the matrix; (ii) the simultaneous excitation of lattice modes. This is the case provided that isolation is really occurring and that dimers or large clusters are not also present in appreciable concentration (*15*). The molecules can occupy positions in the lattice which are energetically similar (perhaps, for example, interstitial and substitutional sites), in which case closely spaced multiple bands will appear, corresponding to a single band in the gas. Annealing may remove all but one of these peaks; this was observed to occur in the TaO spectrum (*13*) and in the $C_3$ spectrum (*16*). In the case of the $C_3$ spectrum the overlapping of the multiple bands in the ultraviolet, at large values of $v'$, makes it difficult to distinguish the individual bands, so the spectrum

Table 1. Identified stellar molecules.

| Class | Temperature* (deg K) | Molecules detected |
|---|---|---|
| C or R, N | 3000 | $C_2$, CN, CH, NH, $SiC_2$, $C_3$, $H_2O$ |
| S | 3000 | ZrO, LaO, YO, SiH, TiO |
| M | 3000 | TiO, VO, MgH, SiH, AlH, ZrO, ScO, YO, CrO, AlO, BO, SiF, SiN, CN, CH, $C_2$ |
| Sun (G2) | 6000 | OH, NH, $O_2$, CH, CN, CO, $C_2$, MgH, SiH, TiO, andCaH [BH, ScO, BO, AlO, ZrO, YO, SiF]†, [$H_2$, NO, SiO, $N_2$ in far-ultraviolet]† |

* Approximate temperature of the photosphere. † Evidence inconclusive.

Table 2. Comparison of gas transitions of $Ti^{16}O$ with neon- and argon-matrix values.

| Gas band system | Gas | | Neon | | Argon | |
|---|---|---|---|---|---|---|
| | λ(Å)* | $\Delta G'_{\frac{1}{2}}$† ($cm^{-1}$) | λ(Å)* | $\Delta G'_{\frac{1}{2}}$† ($cm^{-1}$) | λ(Å)* | $\Delta G'_{\frac{1}{2}}$† ($cm^{-1}$) |
| $\gamma[A^3\Phi_2 - X^3\Delta_1]$ | 7130.4 (14020.6) | 859.8 | 7104 (14073) | 855 | 7253 (13784) | 835 |
| $\gamma[^3\Pi_0 - X^3\Delta_1]$‡ | 6174 (16192) | 862.2 | 6124 (16325) | 863 | 6254.5 (15984) | 843 |
| $\alpha[C^3\Delta_1 - X^3\Delta_1]$ | 5167.36 (19339.4) | 829.8 | 5137.5 (19459) | 830 | 5241.5 (19073) | 828 |

* Values in parentheses are corresponding values in waves per centimeter. † $\Delta G'_{1/2}$ is the vibrational frequency in the excited electronic state. ‡ See *8*.

is made much simpler by annealing at 12°K. The (0,0) band at 4057 angstroms retains a large hump on the high-frequency side, with a maximum at about 30 $cm^{-1}$ from the sharp peak. This hump is attributed to combination of the 4057-Å band with lattice modes, which show up as this strong shoulder after multiple sites have been eliminated.

A striking proof of the multiple-site hypothesis is obtained from the electron-paramagnetic-resonance spectra of atoms trapped in matrices. More important, such spectra at 4°K provide a sensitive indication of the electronic properties of the molecule in its ground state.

## Electron-Paramagnetic-Resonance Spectroscopy

Although other workers have investigated the electron-paramagnetic-resonance spectra of trapped radicals in various media, Jen, Foner, Cochran, and Bowers appear to have been the first to make a concerted attack upon so-called "matrix-isolated" radicals (*17, 18*). Their investigations do not include study of high-temperature molecules, but the conclusions reached from their trapping of hydrogen, nitrogen, and sodium atoms in argon at 4°K are very relevant to a discussion of matrix phenomena.

Figure 4 shows schematically the most recent apparatus, including a furnace with water-cooled electrodes, for the vaporization of high-temperature molecules up to 3000°K. Instead of a furnace, the source of radicals may be a gas discharge, or radicals may be produced in situ in the matrix through dissociation of trapped precursors with ultraviolet light. The dewar flask design is that of Jen *et al.* (*17*), but with certain important modifications, touched upon below. The matrix is laid down on the sapphire rod, which has been cooled to 4°K in a manner similar to that shown in Fig. 1. After the matrix is formed, the rod is lowered by a special device (*19*) into the center of an electron-paramagnetic-resonance cavity, where the species in the matrix are subjected to magnetic, microwave, and radio-frequency fields in the usual manner. In this way, the spin-resonance spectra of trapped atoms and radicals, such at $CH_3$ and $NH_2$, were studied by Jen *et al.* (*20*).

Their result for sodium atoms in matrices is given in Fig. 5 (see *18*). Because the nuclear spin of $Na^{23}$ is $I = 3/2$, one expects to find four (that is, $2I + 1$) lines in the spectrum, as indicated at the top of Fig. 5. However, as one can see from the argon matrix result and more clearly from the enlarged view of the ($M_I = ½$) component, each of the four lines appears to be split into five in the matrix. Jen *et al.* have found that slow warming of the argon matrix from 4° to 40°K causes the sequential disappearance of the lines in each group, beginning with those at the highest magnetic field. From this evidence we may conclude that several trapping sites are available for the sodium atoms in the matrix.

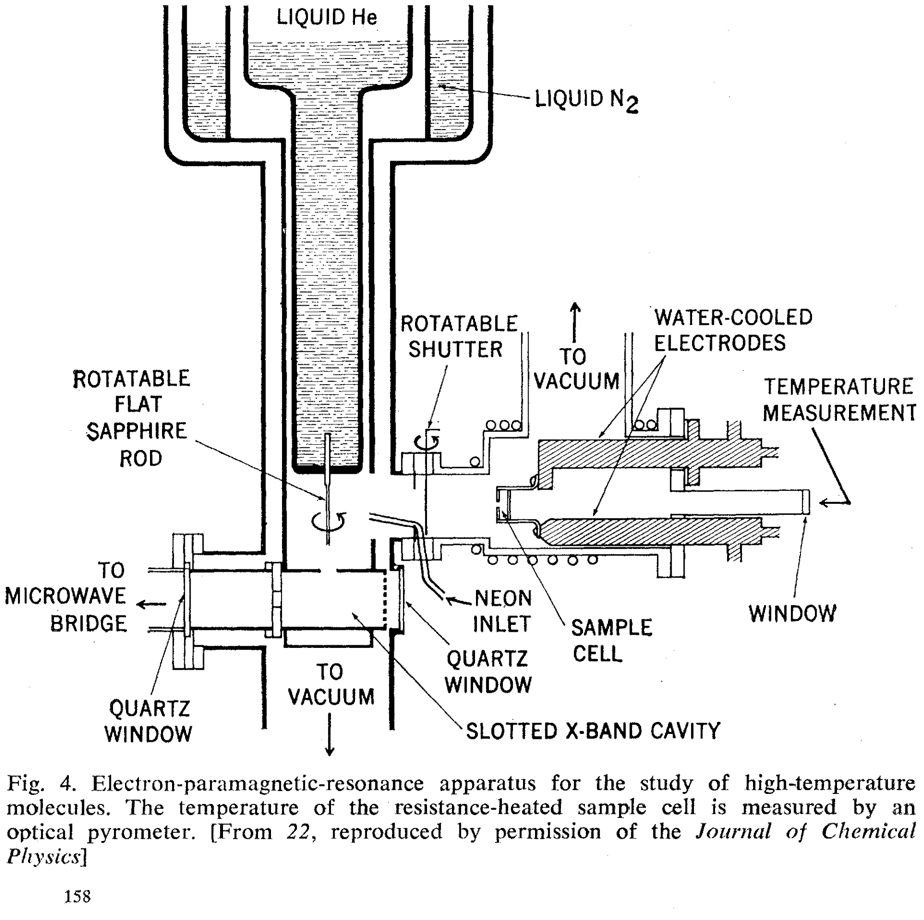

Fig. 4. Electron-paramagnetic-resonance apparatus for the study of high-temperature molecules. The temperature of the resistance-heated sample cell is measured by an optical pyrometer. [From *22*, reproduced by permission of the *Journal of Chemical Physics*]

In the apparatus of Fig. 4, Kasai, Whipple, and Weltner have vaporized molybdenum atoms at 2000°K and have trapped them in a neon matrix at 4°K (*21*). These are rather stringent conditions, and since the magnetic-resonance spectrum showed that isolation had been achieved, the experiment indicates the generality of the application of this technique to high-temperature species. Although molybdenum atoms could be trapped in neon on the sapphire rod, it was found that the smaller, easily diffusing hydrogen atoms could not be; the more rapidly quenched argon matrix was needed for isolating hydrogen atoms at 4°K.

By means of such investigations, a recent discovery has been made concerning the preferential orientation of molecules in matrices. Although not yet extensively utilized in the study of molecules, it has great potentialities (*22*). An "important modification" to the dewar of Jen *et al.* is, simply enough, the installation of a flat rotatable sapphire rod in place of a fixed cylindrical one (see Fig. 4). A matrix formed on this rotatable substrate provides many of the advantages of working with single crystals of the molecules being trapped. The importance of the discovery of oriented molecules is demonstrated by the fact that the preparation of real single crystals of the high-temperature molecules considered here is, of course, quite impossible.

## Transition Metal Oxides: Molecules in Class S and M Stars

Many of the diatomic molecules identified in stars of classes S and M are formed from elements in the section of the periodic table shown in Table 3. They contain the transition metal elements with one to four *d* electrons. The molecules indicated below the heavy line in Table 3 do not appear in stars but are of technological importance, particularly those formed from tantalum, molybdenum, and tungsten.

Theoretical understanding of the electronic properties of these molecules was lacking until recently, when the computations of Carlson, Nesbet, and Moser on TiO (*23*) and of Carlson, Ludeña, and Moser on ScO (*24*) were reported. Such calculations are difficult because of the large number of electrons in the heavy elements. Large computers are necessary, and, even with these, computations have been made only for the oxides of the transition metals involving $3d$ electrons. We cannot consider the calculations here, but I can give a general idea of the results by discussing a simple model, in which the molecules are considered as molecular examples of crystal-field or ligand-field theory. This approach was first taken by Berg and Sinanoglu (*25*), by Hougen, Leroi, and James (*26*), and by Jørgensen (*27*).

If we consider the TiO molecule as being very ionic—that is, as $Ti^{++}$ $O^{--}$— (which it is not), then two of the four outer $3d$ and $4s$ electrons on the titanium would be transferred to the oxygen, two being left on the $Ti^{++}$ ion. But the $Ti^{++}$ ion lies in the strong field of the adjoining $O^{--}$ ion, and that field affects its energy levels; in fact the five $3d$ levels of titanium which formerly had the same energy—that is, which were degenerate—are now split into three increasingly energetic levels—$\delta$, $\pi$, and $\sigma$. [The symbols indicate orbital angular moments of $\pm 2$ $(h/2\pi)$, $\pm 1$ $(h/2\pi)$, and 0 $(h/2\pi)$, respectively.] One would then place the two electrons in the $\delta$ level, but it turns out that interelectronic repulsion and the true covalent nature of the bond cause them to go into the $\delta$ and $\sigma$ levels instead. The occupation of those levels yields the proper configuration of electrons to give the correct ${}^3\Delta_r$ ground state for TiO (see *28*).

One can then proceed across the periodic table by placing additional electrons in the available orbitals. Table 3 gives the ground states of the diatomic oxides which were arrived at from this modified model, together with the results of other calculations of Carlson *et al.* (*29*) and the observations on ZrO and TaO discussed below. With these considerations in mind, let us turn to the experimental work at 4°K and its interpretation.

*Scandium oxide, yttrium oxide, lanthanum oxide.* The ground states of the three molecules ScO, YO, and LaO have been assigned, rather unbelievably, as ${}^4\Sigma$, ${}^2\Sigma$, and ${}^4\Sigma$, respectively, from rotational analysis of their gas emission spectra (*30*). This variation in the assignments results from a splitting appearing in the spectra of ScO and LaO, attributed to spin-spin interaction, which is not discernible in YO. However, it is difficult to account theoretically for a quartet lowest state for these molecules, and the calculations of Carlson *et al.* (*24*) place the ${}^4\Sigma$ level in ScO quite high in energy. During the past year there has been a flurry of activity directed toward establishing the correct ground states (*31*). Several authors have conjectured that the observed splittings arise from nuclear hyperfine interaction, since the nuclear moments of lanthanum and scandium are very large while the nuclear moment of yttrium is relatively small.

These molecules were observed by optical and electron-paramagnetic-resonance spectroscopy in argon matrices at 4°K (*32*). The optical spectra were in essential agreement with the gas spectra, and thus it was demonstrated that the lowest state observed in emission is indeed the ground state in each case. However, the resonance spectra showed clearly that the ground state is, in all cases, ${}^2\Sigma$, and they accounted quantitatively for the optical splittings as nuclear hyperfine-separations, as may be seen in Table 4. There a comparison is given of the splittings observed in the gas spectra with those calculated from the zero-field splittings (A values) obtained in the resonance spectra at 4°K. The A values vary slightly with the matrix gas used, and the trend indicates that the values found in an argon matrix are upper limits to what would be expected in the gas, as is

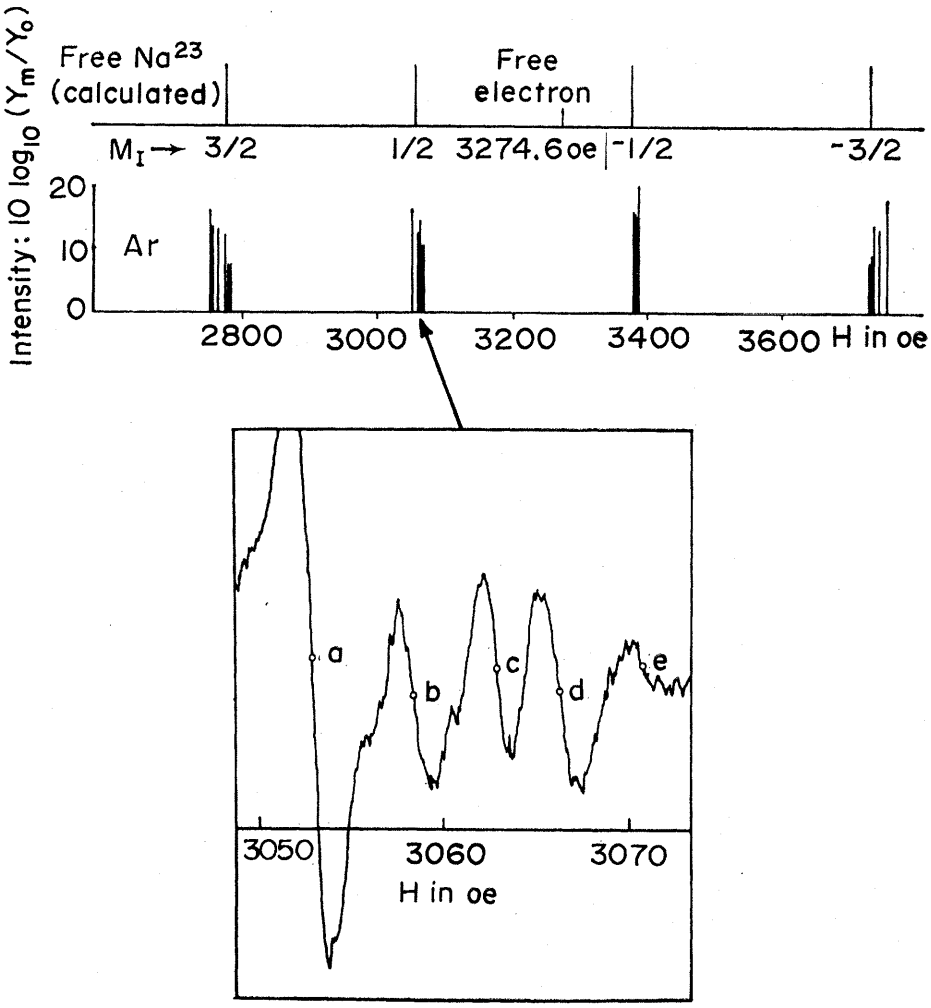

Fig. 5. Electron-paramagnetic-resonance spectrum of sodium atoms in an argon matrix at 4°K. (Top) Calculated spectrum for free atoms; (bottom) multiple-site effect upon the spectrum. [From *18*, reproduced by permission of C. K. Jen *et al.* and of *The Physical Review* (*59*)]

seen to be the case in the data of Table 4. The odd electron is shown to have essentially *s*-shell character, in agreement with theory.

The solution to this problem is thus provided by work at 4°K, and it is difficult to see how it could have been as expeditiously arrived at by any other method.

*Titanium oxide, zirconium oxide, hafnium oxide.* The properties of TiO discussed above have been established by the well-known work of Phillips, Christy, and others on gas spectra (*9*, *33*). Titanium oxide was investigated optically at 4°K in an effort to check the agreement of results for matrix and gas (Table 2 and Fig. 3), but the matrix measurements (*8*) also serve to confirm Phillips's findings of a triplet lowest state.

Linevsky's (*7*) infrared study of ZrO in an argon matrix at 4°K probably provided the first evidence that the ground state of ZrO is not the same as that of TiO, or perhaps one should say that his study made it necessary to reconsider Afaf's much earlier assumption of a $^1\Sigma^+$ ground state (*34*). The electronic absorption spectrum of ZrO was measured in neon matrices at 4°K by Weltner and McLeod (*8*), who found that only the singlet-singlet transitions were observed. This finding, coupled with the matrix work in the infrared, makes it certain that the ground state of ZrO is $^1\Sigma^+$. The infrared spectrum at 4°K gave a vibrational frequency of 975 cm$^{-1}$ for ZrO, a value which does not agree with the 931 cm$^{-1}$ obtained in the gas spectrum for the $^3\Delta_r$ state but which does agree nicely with the gas-spectrum value of 969.7 cm$^{-1}$ for the $^1\Sigma^+$ state.

It is well known that the transition metals in the second and third periods of the periodic table are more alike than those in the first and second periods, because the 4*f* shell is filled between the second and third periods and shields the increase in nuclear charge. For this reason one would expect HfO to resemble ZrO and to have a $^1\Sigma^+$ ground state. That this is the case has not been proved, since the gas spectrum of HfO has not been rotationally analyzed (*35*), but the resemblance is confirmed by the closeness of the HfO vibrational frequency, 974 cm$^{-1}$, to the ZrO vibrational frequency, 975 cm$^{-1}$, in a neon matrix (*8*). Hafnium oxide has apparently not been observed in stars.

*Vanadium oxide, niobium oxide, tantalum oxide.* The ground state of VO is not definitely known, but it is most probably either $^2\Delta_r$ or $^4\Sigma^-$. The bands observed in the gas spectrum have been analyzed to yield a $^2\Delta$ lower state, but doubt about this assignment has been expressed by Lagerqvist in his latest discussion of the spectrum (*36*). Reminiscent of the ScO series, vanadium also has a large nuclear magnetic moment ($\mu = +5.1478$, $I = 7/2$), and this source of additional lines in the spectrum has to be considered in the analysis. However, recent refined theoretical calculations (*29*) indicate that the lowest state is $^4\Sigma^-$, and the electron-paramagnetic-resonance spectra at 4°K (*12*) appear to support these calculations; consequently I have indicated the VO ground state to be $^4\Sigma^-(\delta^2\sigma)$ in Table 3. That the lower state in the gas spectrum is the ground state is confirmed by the optical spectrum at 4°K, since two strong matrix progressions, at 7904 and 5708 Å, have been observed in the gas. [A weak progression at 4185 Å has not been reported in the gas (*12*).]

Table 3. Ground states of transition-metal oxides. The ground states and configurations underlined are predicted.

| | | | |
|---|---|---|---|
| **ScO**<br>$^2\Sigma(\sigma)$ | **TiO**<br>$^3\Delta_r(\delta\sigma)$ | **VO**<br>$\underline{^4\Sigma^-(\delta^2\sigma)}$ | **CrO**<br>$\underline{^3\Sigma^-(\delta^2)}$ |
| **YO**<br>$^2\Sigma(\sigma)$ | **ZrO**<br>$^1\Sigma^+(\sigma^2)$ | **NbO**<br>$\underline{^2\Delta_r(\sigma^2\delta)}$ | **MoO**<br>$\underline{^3\Sigma^-(\delta^2)}$ |
| **LaO**<br>$^2\Sigma(\sigma)$ | **HfO**<br>$\underline{^1\Sigma^+(\sigma^2)}$ | **TaO**<br>$^2\Delta_r(\sigma^2\delta)$ | **WO**<br>$\underline{^3\Sigma^-(\delta^2)}$ |

Table 4. Nuclear hyperfine-structure separations ($\Delta\nu$) of ScO, YO, and LaO.

| Compound | Optical spectra* (cm$^{-1}$) | Electron paramagnetic resonance at 4°K (argon matrices)† (cm$^{-1}$) |
|---|---|---|
| ScO | 0.21 | 0.27 |
| YO | .0‡ | .03 |
| LaO | .48 | .52 |

* See *30*. † See *32*. ‡ The optical splitting was so small here as to be undetectable.

The molecules TaO and $TaO_2$ have been observed in neon and argon matrices and exemplify a case where low-temperature spectra have made a significant contribution (*13*). Neither of these molecules has been observed in stars, but they are evolved from hot tantalum metal in an oxygen atmosphere. The ground state of TaO was established as $^2\Delta_r$ when the 4°K spectra were compared with the gas-phase spectra as analyzed by Premaswarup and Barrow (*37*). Also, 13 additional electronic states were observed in the low-temperature absorption spectra. A strong band system of $TaO_2$, not previously observed in the gas, was found at 8706 Å in neon, and a partial vibrational assignment of the excited and ground states could be made.

Niobium oxide was not studied at low temperatures, largely because earlier gas-phase work indicated that NbO was similar to TaO, also having a $^2\Delta$ ground state (*38*). However, the fruitful investigation of TaO indicates that a study of NbO at 4°K would also be worth while.

*Chromium oxide, molybdenum oxide, tungsten oxide.* Several attempts were made to observe the spectrum of CrO in neon matrices at 4°K, but until now only features due to chromium atoms have been observed, between 8900 and 2000 Å or in the electron-paramagnetic-resonance spectrum. At present there is, then, no evidence to indicate that the lower state of the assigned $A^5\Pi \leftrightarrow X^5\Pi_i$ transition observed by

Ferguson, Ghosh, and Ninomiya (*39*) really involves the ground state of CrO. This observation is in agreement with a ground state of $^3\Sigma^-$ (see Table 3) derived from recent, still tentative, calculations (*29*).

The diatomic molecules, MoO and WO, have been observed in gas-emission spectra, but neither spectrum has been satisfactorily analyzed (*40*). Tungsten oxide has been observed optically in matrices at 4°K and found to yield a very rich spectrum between 3500 and 6000 Å (*41*). Particularly noteworthy was the number of vibrational perturbations in the spectrum of $W^{16}O$; such perturbations often disappeared when $W^{18}O$ was examined. Perhaps these perturbations account for part of the difficulty in analyzing the gas spectrum. The matrix spectra indicated that the band system at 4806.4 Å in the gas spectrum [(0,0) band at 4807 Å in neon] was essentially unperturbed in both molecules and involves the ground state, properties which make this system a good candidate for any future attempt to analyze the gas spectrum.

In the matrix work, a good spectrum of $WO_2$ was also observed at 7890 Å, very similar to the spectrum of $TaO_2$. The gas spectrum of the $WO_2$ molecule, like that of the $TaO_2$ molecule, has not as yet been observed. Other, larger tungsten-oxygen molecules can dominate the gas phase when oxygen is passed over tungsten at lower temperatures, or if the higher solid oxides are vaporized, and $W_4O_{12}$, $W_3O_9$, $W_3O_8$, $W_2O_6$, and $WO_3$ have all been identified in mass spectrometric work. These molecules have also been trapped at 4°K and observed in the infrared spectral region, but efforts to attribute specific bands to specific molecules have been only partially successful. Such attribution is difficult, but it seems unlikely that an unraveling of the vibrational spectra of these molecules can be accomplished in any other way. The similarity of the molybdenum system to the tungsten system indicates that the same situation is to be met there.

## Molecules in Carbon Stars (Classes R and N)

Carbon stars, in general, are composed of the light elements hydrogen, carbon, nitrogen, and oxygen. The diatomic molecules $C_2$, CN, NH, and CH have all been studied by optical spectroscopy of the gas, some of them being produced in high-temperature furnaces, others by flash photolysis. Many of them have been observed in matrices at 4°K, in work discussed by Pimentel and Ramsay (see *4*). Although the matrix experiments are interesting and relevant to this discussion, the information obtained about the diatomic molecules themselves has generally not added much to what was already known. Diatomic $C_2$ is an anomalous case, since the perturbations by the matrices are difficult to comprehend; in fact, $C_2$ has been rather a "thorn in the side" of advocates of matrix studies. I consider it briefly after discussing $C_3$ and $SiC_2$, two molecules which have perplexed spectroscopists for many years.

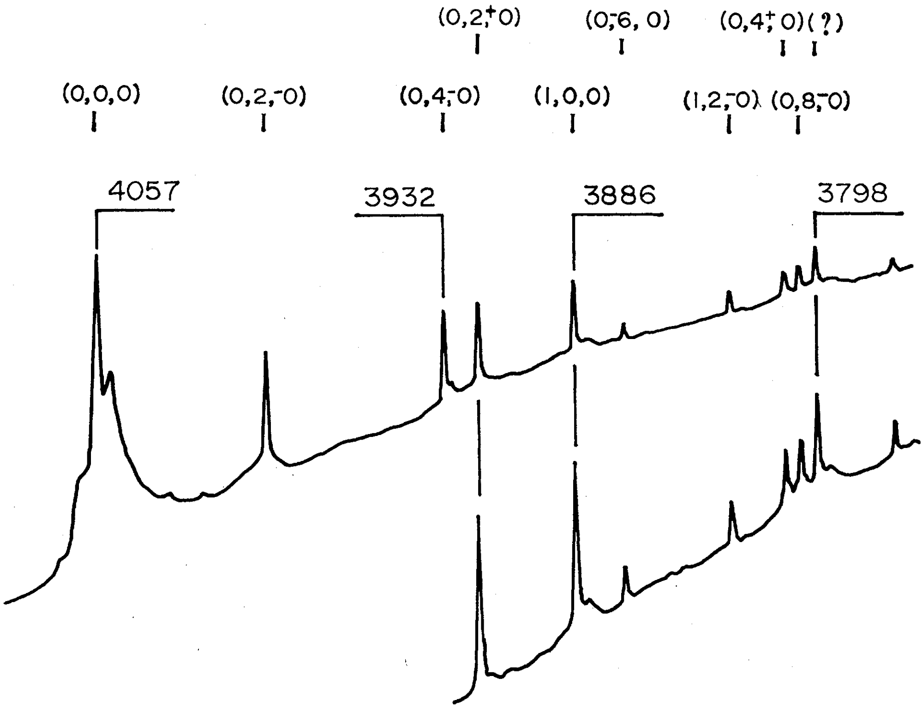

Fig. 6. A portion of the absorption spectrum of an annealed neon matrix of $C_3$ at 4°K. Symbols at the top indicate the assignments of the bands to particular vibronic levels in the excited $^1\Pi_u$ state. Wavelengths are in angstroms.

The study of $C_3$ has a particularly interesting history, which I will not go into here except to say that only recently has the complicated gas spectrum beginning at about 4050 Å been analyzed. The observation of a "cold" spectrum during the flash photolysis of diazomethane enabled Gausset, Herzberg, Lagerqvist, and Rosen to clarify the situation (*42*), and their analysis represents a real tour de force in molecular spectroscopy. The difficulties arose principally because of a very large vibronic (Renner) effect in the upper state of the $^1\Pi_u \leftarrow X^1\Sigma^+_g$ transition and because of the extraordinarily small value (63 $cm^{-1}$) for the ground-state bending frequency of $C_3$. The latter circumstance leads to the excitation of many transitions—that is, to "hot" bands—at high temperatures, considerably complicating the spectrum. Hence, $C_3$ is an ideal case for study at 4°K.

There are many sites of slightly different energy for $C_3$ in a neon matrix, which lead to a complicated band shape, but they can be annealed out by holding the matrix at 11° to 12°K for a time. A portion of the electronic absorption spectrum in neon at 4°K after annealing is shown in Fig. 6, together with the assignments of the observed bands (*16, 43*). As contrasted with the usual triatomic molecule, the spacings of these bands are very irregular, due to the large Renner parameter, $\epsilon$, which represents the degree of coupling between the electronic and the bending vibrational motions. In the gas phase, Gausset *et al.* have found that $\epsilon = +0.537$ and $\omega'_2$ (the bending frequency in the upper state) $= 307.9$ $cm^{-1}$. These parameters may be used to calculate the positions of the vibronic transitions expected in the matrix spectrum, and to make a comparison with the observed values. When this is done, it is found that essentially every band in the matrix spectrum out to 3500 Å can be accounted for, if combinations with $\nu'_1 = 1090$ cm$^{-1}$ are also included ($\nu'_1$ is the symmetric stretching frequency in the excited state).

What contribution has work at 4°K made to the characterization of the $C_3$ molecule, other than confirming the large Renner effect by accounting for bands farther into the ultraviolet? It has supplied the remaining unknown ground state vibrational frequencies: $\nu''_3 = 2040$ cm$^{-1}$ from infrared measurements, and $\nu''_1 = 1235$ cm$^{-1}$ from fluorescence spectra. The infrared band is shown in Fig. 7, with the splitting into six bands when a carbon sample containing $^{13}C$ is vaporized. The isotope effect leaves no doubt that we are observing an isolated $C_3$ molecule. Table 5 gives a summary of the present state of knowledge of $C_3$ in the $^1\Pi_u$ state and ground state, $^1\Sigma^+_g$, as determined from gas-phase and matrix work.

Table 5. Properties of the $C_3$ molecule.

| $v_1$ (cm$^{-1}$) | $v_2$ (cm$^{-1}$) | $v_3$ (cm$^{-1}$) |
|---|---|---|
| | *Ground electronic state, $^1\Sigma^+_g$ | |
| 1235 | 63 | 2040 |
| | †*Excited state,* $^1\Pi_u$ | |
| 1085 | 307.9 | ? |

* C-C distance 1.277 Å. † C-C distance, 1.305 Å; Renner parameter, 0.537.

Other excited electronic states of $C_3$ are also of interest, and at least one of these has been observed in matrices. A strong long-lived (0.02 second) emission at 5865 Å was observed when $C_3$ in neon at 4°K was excited by mercury light. It is believed that this is emission from a low-lying triplet state to the ground state, $^1\Sigma^+_g$ (*44*). Recently the absorption spectrum in neon was extended out to 2000 Å in an effort to detect the $^1\Sigma^+_u \leftarrow X^1\Sigma^+_g$ transition of $C_3$ which was expected to appear strongly in that region. But even though the 4050-Å system was quite intense, no other strong band system was observed (*45*).

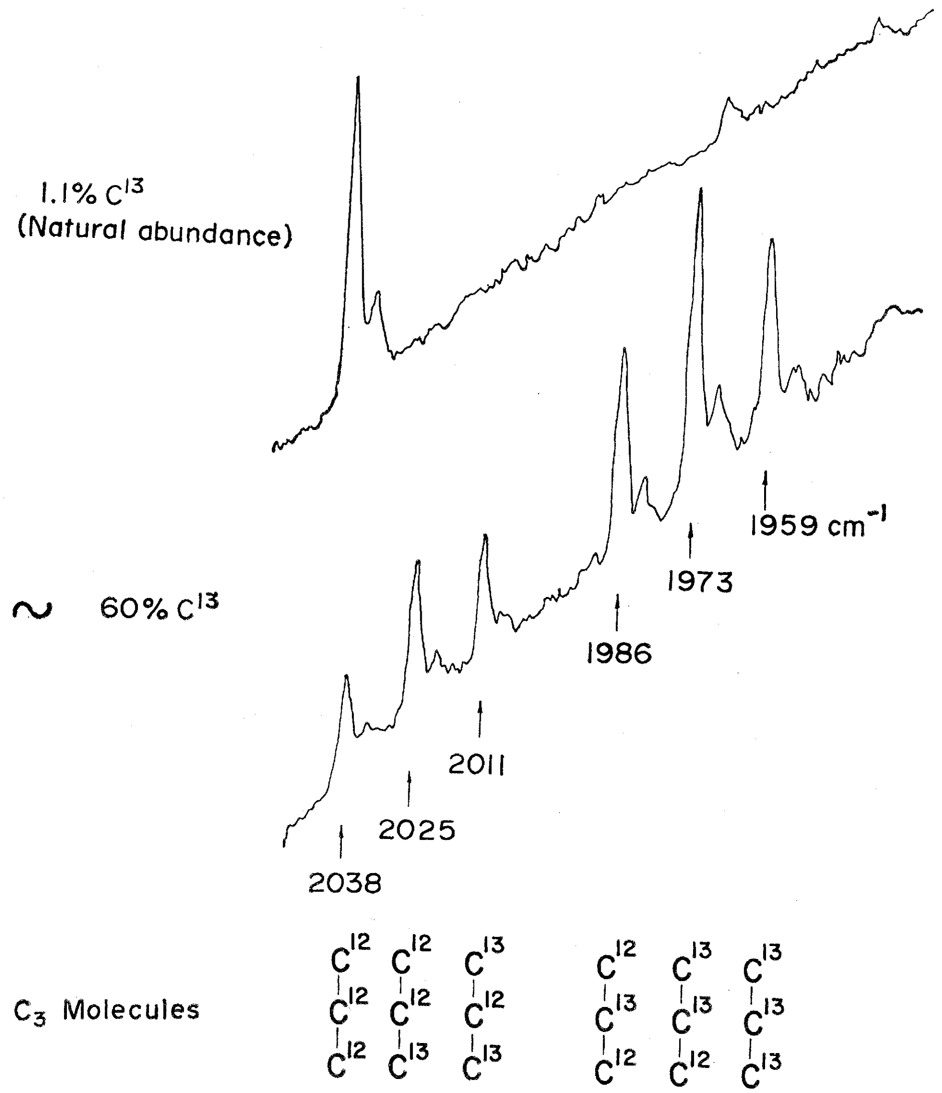

Fig. 7. Infrared spectrum of $C_3$ in an argon matrix at 20°K. (Top curve) $\nu_3$ band of $^{12}C_3$. (Bottom curve) $\nu_3$ bands of the six isotopically substituted $C_3$ molecules shown. [From *44*, reproduced by permission of the *Journal of Chemical Physics*]

The $SiC_2$ molecule appears as a blue-green emission in carbon stars (*46*). Evidence that $SiC_2$ is the emitter was given by Kleman (*47*), who first produced it in the laboratory. A King furnace was used in which the carbon tube, containing silicon, was heated to about 2500°K. The bands were broad at this temperature, and rotational analysis was not possible. However, vibrational analysis indicated a frequency of $\nu''_3 = 1742$ cm$^{-1}$ in the ground state, dropping to $\nu'_3 = 1460$ cm$^{-1}$ in the excited state. This frequency was so high that it essentially required the presence of a C—C unit in the molecule. Other features of the spectrum, together with the known presence of silicon, indicated that the molecule was $SiC_2$ with the unsymmetrical linear structure, $Si{=}C{=}C$.

The 4°K spectrum was measured on a neon matrix prepared by trapping the molecules vaporizing from solid silicon carbide at about 2800°K (*14*). Mass spectrometry (*48*) had previously established the vapor to be largely silicon atoms, with $SiC_2$ and $Si_2C$ each present in the proportion of about 8 percent. The (0,0) band of $SiC_2$ was observed to occur at 4963 Å, as compared with 4977.1 Å in the gas, an observation which supports Kleman's identification. The bands are, again, quite broad (annealing might have helped); however, their distinctive shape makes identification of those belonging to $SiC_2$ easy. Improved vibrational assignments resulted from the matrix study, but an anomalous anharmonicity of $\nu_1$ and $\nu_2$ was observed which marred the credibility of the assignment for the upper state. There was evidence of the presence of another molecule, perhaps $Si_2C$, which may be a stellar molecule, and the spectrum of what we believe to be the previously unobserved $Si_2C_3$ molecule was also analyzed.

A few words about $C_2$ at 4°K are in order, since it is a unique and puzzling case. It is important, since the interpretation of the matrix spectra indicates that the molecule is trapped in an electronic state other than its ground state at 4°K.

Gaseous $C_2$ has been studied thoroughly, and recently a summary of its properties has been published by Ballik and Ramsay (*49*). These authors were the first to establish that it has a $^1\Sigma^+_g$ ground state and that the $^3\Pi_u$ state lies about 610 cm$^{-1}$ higher. All seems to be as expected for the gas molecule. However, when it is trapped in argon at 4° or 20°K, the Swan bands ($^3\Pi_g \leftarrow {}^3\Pi_u$)—or at least bands that are thought to be the Swan bands—appear in absorption. These observations were first reported by McCarty and Robinson (*50*) and have since been essentially confirmed by a number of authors (*51, 52*). The implication is that a large number of the $C_2$ molecules are trapped in the excited $^3\Pi_u$ state, which is stable in the matrix for hours or even days. In other words, the matrix has now made the $^3\Pi_u$ state of $C_2$ more stable than the $^1\Sigma^+_g$ state. Effects such as this have not been observed for other molecules in matrices (*53*), and, furthermore, the vibrational frequencies in the excited state show a strange variation with the matrix used: $\nu'$, in the gas, = 1750 cm$^{-1}$; in neon, 2094; in argon, 2053 (*54*); and in xenon, 1940. This is indeed strange behavior when compared with results obtained from other matrix spectra.

All the evidence is rather unbelievable in view of the matrix work on other gases. To me it seems most likely that the Swan bands of $C_2$ are not being observed at all but that another carbon molecule (perhaps $C_4$ or $C_5$) is responsible for the absorption spectrum in that region. Recent careful diffusion experiments in our laboratory on a neon matrix containing carbon vapor support that conclusion (*16*).

## Conclusions

Optical spectroscopy of stellar molecules trapped at 4°K is particularly valuable when the data can be used to complement the corresponding gas data. The ground state is then directly established by measurement of the absorption spectrum at the low temperature, since all transitions beginning from excited states are eliminated. Isotopic substitution establishes the (0,0) bands of transitions to excited electronic states, and when these data are combined with infrared and fluorescence measurements at 4°K, most of the vibrational properties of the ground and excited states can be obtained. Of the many examples cited and discussed here, $C_3$ is perhaps the most outstanding.

Because the various molecules trapped in matrices are usually identified through prior mass spectrometric work, the optical observations often lead to the discovery of band systems of molecules whose spectra have not previously been observed—for example, those of $Si_2C_3$, $TaO_2$, and $WO_2$. In these cases the location of the spectral regions in which molecular transitions appear may also serve to encourage the gas spectroscopist to further exploration with high-dispersion spectrographs.

I share Ramsay's view (*4*, p. 204) that further investigation of *f*-number determinations from matrix spectra should be encouraged, particularly because of the lack of such data for molecules in stars. The principal source of error probably lies in the estimation of the number of molecules per square centimeter in the matrix, but no real test of this has been made. The only existing *f* values from matrix spectra are those for the $C_3$ (*43, 44*) and $C_2$ (*51*) molecules, and these are not ideal for test purposes. Because of the anomalous nature of the matrix results discussed above, the rather good agreement between *f* values for the solid and gas phases of $C_2$ (*51*) cannot be considered as support for the matrix determinations. What is needed is a matrix determination of several $f_{v'v''}$ values (that is, determinations for specific bands) for molecules such as CN and NO or, preferably, for a gas vaporized at high temperature, for which these *f* values are relatively well established in the gas phase.

In this connection the possibility of determining other molecular properties in matrices comes to mind. However, it has been clearly shown that the shape of the potential energy function in the electronic states of molecules can be affected when molecules are trapped in matrices. Brewer, Brabson, and Meyer, in work on $S_2$ (*55*), and Schnepp and Dressler, in work on $O_2$ (*56*), have examined the anharmonicity in matrices over many vibrational levels. Distortion of the gas potential energy curves occurs in the heavier matrices and sometimes at high vibrational levels in the light ones. Recently work has been begun on comparing the Franck-Condon factors connecting the ground state and two excited states of ScF trapped in a neon matrix (*57*) with factors calculated from the gas-spectrum data of R. F. Barrow *et al.* (*58*) ($\Delta r_e$, the change in interatomic distance upon excitation, has a relatively large value of $\sim 0.1$ Å in these systems). As is well known, such factors are particularly sensitive to the value of $\Delta r_e$, but differences in anharmonicity do not, however, have as significant an effect upon the Franck-Condon factors. Hence a comparison of the matrix and gas factors will lead to further information about matrix effects and will indicate whether Franck-Condon factors can be obtained from matrix spectra.

One of the important problems in the study of stellar molecules is the determination of the low-lying electronically excited states, similar to the $^1\Delta \leftrightarrow X^3\Delta$ difference ($\sim$ 580 cm$^{-1}$) in TiO measured by Phillips. Most of the transition-metal oxides have such low-lying levels, and they must be taken into consideration in any calculation of thermodynamic effects at high temperature. It appears that the study of emission spectra in the infrared at 4°K may be one approach to this problem, and an attempt is now being made to confirm the TiO value in order to test the method.

Perhaps the greatest advantage of matrix-isolation is the fact that it allows study of these molecules—or of any molecules difficult to produce in a microwave cavity—by electron-paramagnetic-resonance spectroscopy. Study of molecules by this means can provide information about ground state wave functions that is not obtainable by optical spectroscopy, as illustrated by the investigation of ScO, YO, and LaO. Also, it seems likely that the preferential orientation of molecules in matrices, which is probably achievable in most cases, will be a valuable asset in the study of the magnetic properties of molecules by electron-paramagnetic-resonance spectroscopy, regardless of whether the molecules are "hot" or "cold" (*60*).

### References and Notes

1. See, for example, L. H. Aller, *Astrophysics, The Atmospheres of the Sun and Stars* (Ronald, New York, ed. 2, 1963); ———, in *Stellar Atmospheres*, J. L. Greenstein, Ed. (Univ. of Chicago Press, Chicago, 1960); P. C. Keenan, *ibid.*, chap. 14; J. L. Greenstein, in *Proceedings of the Xth Colloquium Spectroscopicum Internationale*, E. R. Lippincott and M. Margoshes, Eds. (Spartan Books, Washington, D.C., 1963).
2. T. Tsuji, *Proc. Japan Acad.* **40**, 99 (1964).
3. An excellent discussion of the vaporization of high-temperature molecules and their properties is given by L. Brewer, in vol. 6 of *Proceedings of the Robert A. Welch Foundation Conferences on Chemical Research* (Robert A. Welch Foundation, Houston, Texas, 1965), pp. 47–92. For a review of the mass spectrometry work on the vapors over refractory solids, see M. G. Inghram and J. Drowart, in *International Symposium on High Temperature Technology* (McGraw-Hill, New York, 1960), and J. Drowart, *Condensation and Evaporation of Solids* (Gordon and Breach, New York, 1964), p. 255.
4. For a detailed discussion see A. M. Bass and H. P. Broida, Eds., *Formation and Trap-*

*ping of Free Radicals* (Academic Press, New York, 1960).

5. For more detailed discussion of experimental procedure see W. Weltner, Jr., and J. R. W. Warn, *J. Chem. Phys.* **37**, 292 (1962); W. Weltner, Jr., P. N. Walsh, C. L. Angell, *ibid.* **40**, 1299 (1964); W. Weltner, Jr., and D. McLeod, Jr., *ibid.*, p. 1305; M. J. Linevsky, *ibid.* **34**, 587 (1961). Some work on the possibilities of sampling from an arc has been done by D. McLeod, Jr., and W. Weltner, Jr.
6. J. Drowart, R. P. Burns, G. DeMaria, M. G. Inghram, *J. Chem. Phys.* **31**, 1131 (1959).
7. M. J. Linevsky, "Proceedings Meeting of The Interagency Chemical Rocket Propulsion Group, Thermochemistry, 1st, New York, 1964," *Chemical Propulsion Inform. Agency Pub. No. 44 (U), Johns Hopkins Appl. Phys. Lab.* (1964).
8. W. Weltner, Jr., and D. McLeod, Jr., *J. Phys. Chem.* **69**, 3488 (1965).
9. A. Christy, *Astrophys. J.* **70**, 1 (1929); F. Lowater, *Proc. Phys. Soc. London* **41**, 557 (1929); F. P. Coheur, *Bull. Soc. Roy. Sci. Liege* **12**, 98 (1943); A. Christy, *Phys. Rev.* **33**, 701 (1929). The work on the $\gamma$ and $\alpha$ systems has been revised by J. G. Phillips, *Astrophys. J.* **111**, 314 (1950); *ibid.* **114**, 152 (1951).
10. Thorough consideration of the effect of matrices on the vibrational frequencies in molecules is given in E. Becker and G. C. Pimentel, *J. Chem. Phys.* **25**, 224 (1956); G. C. Pimentel, *Pure Appl. Chem.* **4**, 61 (1962); G. C. Pimentel and S. W. Charles, *ibid.* **7**, 111 (1963).
11. E. Catalano and D. E. Milligan, *J. Chem. Phys.* **30**, 45 (1959); J. A. Glasel, *ibid.* **33**, 252 (1960); R. L. Redington and D. E. Milligan, *ibid.* **39**, 1276 (1963); D. W. Robinson, *ibid.*, p. 3430; D. E. Milligan, R. M. Hexter, K. Dressler, *ibid.* **34**, 1009 (1961); A. Cabana, G. B. Savitsky, D. F. Hornig, *ibid.* **39**, 2942 (1963); L. J. Schoen, D. E. Mann, C. Knobler, D. White, *ibid.* **37**, 1146 (1962); D. W. Robinson and W. G. Von Holle, *ibid.* **44**, 410 (1966). For the most recent theoretical discussion, see H. Friedmann and S. Kimel, *J. Chem. Phys.* **43**, 3925 (1965).
12. Optical work on VO has been carried out by W. Weltner, Jr., and D. McLeod. Electron-paramagnetic resonance work has been done by P. H. Kasai.
13. W. Weltner, Jr., and D. McLeod, Jr., *J. Chem. Phys.* **42**, 882 (1965).
14. ———, *ibid.* **41**, 235 (1964).
15. G. C. Pimentel and S. W. Charles, *Pure Appl. Chem.* **7**, 111 (1963); K. B. Harvey, H. F. Schurvell, J. R. Henderson, *Can. J. Chem.* **42**, 911 (1964).
16. See W. Weltner, Jr., and P. N. Walsh, *J. Chem. Phys.* **37**, 1153 (1962); ———, C. L. Angell, *ibid.* **40**, 1299 (1964); W. Weltner, Jr., and D. McLeod, Jr., *ibid.*, p. 1305. The term *annealing* is here used to imply relieving of strain, with perhaps some solid-state diffusion.
17. C. K. Jen, S. N. Foner, E. L. Cochran, V. A. Bowers, *Phys. Rev.* **112**, 1169 (1958).
18. C. K. Jen, V. A. Bowers, E. L. Cochran, S. N. Foner, *ibid.* **126**, 1749 (1962).
19. W. H. Duerig and I. L. Mador, *Rev. Sci. Instr.* **23**, 421 (1952).
20. A review of the electron-paramagnetic-resonance work done by the Johns Hopkins group is given by C. K. Jen in *Formation and Trapping of Free Radicals*, A. M. Bass and H. P. Broida, Eds. (Academic Press, New York, 1960).
21. P. H. Kasai, E. B. Whipple, W. Weltner, Jr., in preparation.
22. ———, *J. Chem. Phys.* **44**, 2581 (1966).
23. K. D. Carlson and C. Moser, *J. Phys. Chem.* **67**, 2644 (1963); K. D. Carlson and R. K. Nesbet, *J. Chem. Phys.* **41**, 1051 (1964).
24. K. D. Carlson, E. Ludeña, C. Moser, *J. Chem. Phys.* **43**, 2408 (1965).
25. R. A Berg and O. Sinanoglu, *ibid.* **32**, 1082 (1960).
26. J. T. Hougen, G. E. Leroi, T. C. James, *ibid.* **34**, 1670 (1961).
27. C. K. Jørgensen, *Mol. Phys.* **7**, 417 (1963).
28. A more complete discussion of the ligand-field model as applied to TiO, ZrO, and HfO may be found in W. Weltner, Jr., and D. McLeod, Jr., *J. Phys. Chem.* **69**, 3488 (1965).
29. K. D. Carlson and C. Moser, *J. Chem. Phys.* **44**, 3259 (1966); Drs. Carlson and Moser have kindly allowed me to use the results of their calculations (still tentative) on CrO in Table 3.
30. L. Åkerlind, *Arkiv Fysik* **22**, 41 (1962); U. Uhler and L. Åkerlind, *ibid.* **19**, 1 (1961); L. Åkerlind, *ibid.* **22**, 65 (1962).
31. R. A. Berg, L. Wharton, W. Klemperer, A. Büchler, J. L. Stauffer, *J. Chem. Phys.* **43**, 2416 (1965); L. Brewer and R. M. Walsh, *ibid.* **42**, 4055 (1965).
32. W. Weltner, Jr., P. H. Kasai, D. McLeod, Jr., in preparation. For a preliminary account of the electron-paramagnetic-resonance work, see P. H. Kasai and W. Weltner, Jr., *J. Chem. Phys.* **43**, 2553 (1965).
33. J. G. Phillips, *Astrophys. J.* **115**, 567 (1952).
34. M. Afaf, *Proc. Phys. Soc. London* **63A**, 1156 (1950).
35. See A. Gatterer, J. Junkes, E. W. Salpeter, B. Rosen, *Molecular Spectra of Metallic Oxides* (Vatican Press, Vatican City, 1957).
36. A. Lagerqvist, *Mem. Soc. Roy. Sci. Liege* **18**, 550 (1957).
37. D. Premaswarup and R. F. Barrow, *Nature* **180**, 602 (1957).
38. U. Uhler, *Arkiv Fysik* **8**, 265 (1954).
39. W. F. C. Ferguson, *J. Res. Nat. Bur. Std.* **8**, 381 (1932); C. Ghosh, *Z. Physik* **78**, 521 (1932); M. Ninomiya, *J. Phys. Soc. Japan* **10**, 829 (1955).
40. T. M. Swaminathan and S. G. Krishnamurty, *Current Sci. India* **23**, 258 (1954); J. C. Howard and J. C. Conway, *J. Chem. Phys.* **43**, 3055 (1965); A. Gatterer and S. G. Krishnamurty, *Nature* **169**, 543 (1952); V. Vittalachar and S. G. Krishnamurty, *Current Sci. India* **23**, 357 (1965).
41. W. Weltner, Jr., and D. McLeod, Jr., *J. Mol. Spectr.* **17**, 276 (1965).
42. L. Gausset, G. Herzberg, A. Lagerqvist, B. Rosen, *Astrophys. J.* **142**, 45 (1965).
43. Work on the 4050-Å system of $C_3$ in many other matrix gases has been done by R. L. Barger and H. P. Broida [*J. Chem. Phys.* **37**, 1152 (1962); *ibid.* **43**, 2364 (1965)].
44. W. Weltner, Jr., and D. McLeod, Jr., *ibid.* **40**, 1305 (1964).
45. W. Weltner, Jr., "Proceedings Meeting of The Interagency Chemical Rocket Propulsion Group, Thermochemistry, 3rd, El Segundo, Calif., 1965," *Chemical Propulsion Inform. Agency Pub. No. 82 (U), Johns Hopkins Appl. Phys. Lab.* (1965).
46. P. W. Merrill, *Pub. Astron. Soc. Pacific* **38**, 175 (1926); R. F. Sanford, *ibid.*, p. 177; C. D. Shane, *Lick Obs. Bull.* **13**, 123 (1928); A. McKellar, *J. Roy. Astron. Soc. Can.* **41**, 147 (1947).
47. B. Kleman, *Astrophys. J.* **123**, 162 (1956).
48. J. Drowart, G. de Maria, M. G. Inghram, *J. Chem. Phys.* **29**, 1015 (1958).
49. E. A. Ballik and D. A. Ramsay, *Astrophys. J.* **137**, 84 (1963).
50. M. McCarty, Jr., and G. W. Robinson, *J. Chem. Phys.* **56**, 723 (1959).
51. R. L. Barger and H. P. Broida, *ibid.* **37**, 1152 (1962); *ibid.* **43**, 2371 (1965).
52. W. Weltner, Jr., P. N. Walsh, C. L. Angell, *ibid.* **40**, 1299 (1964); L. J. Schoen, paper presented at the International Symposium on Free Radicals, 5th, Uppsala, 1961.
53. A few other claims have been made of absorption of energy from excited levels in matrices [see G. W. Robinson, in *Methods of Experimental Physics*, D. Williams, Ed. (Academic Press, New York, 1962), vol. 3, p. 233], which can only be justified by the assumption of optical pumping of the molecules to occupy the upper state. This assumption requires either that there be an intense source of light or that the excited level have a relatively long lifetime. In my opinion, proof that optical pumping actually occurs in these cases is lacking. In the case of absorption from excited rotational states of $NH_2$, C. K. Jen (*4*, p. 238) gives an alternative explanation of the observations.
54. This value is given as 1920 $cm^{-1}$ by Barger and Broida and by McCarty and Robinson. The shape and behavior of our band at 4700 Å is not in accord with this derived frequency, so we continue to give 2053 $cm^{-1}$ as the value in argon.
55. L. Brewer, G. D. Brabson, B. Meyer, *J. Chem. Phys.* **42**, 1385 (1965).
56. O. Schnepp and K. Dressler, *ibid.*, p. 2482.
57. D. McLeod, Jr., and W. Weltner, Jr., *J. Phys. Chem.*, in press.
58. R. F. Barrow, W. J. M. Gissane, R. C. LeBargy, G. V. M. Rose, P. A. Ross, *Proc. Phys. Soc. London* **83**, 889 (1964); R. F. Barrow and W. J. M. Gissane, *ibid.* **84**, 615 (1964).
59. Figure 5 was kindly supplied by Dr. C. K. Jen.
60. *Note added in proof.* Since this article was submitted for publication, a few relevant papers have been published. On $C_2$ and $C_3$, W. Weltner, Jr., and D. McLeod, Jr., *J. Chem. Phys.* **45**, 3096 (1966); on Frank-Condon factors in matrices, D. McLeod, Jr., and W. Weltner, Jr., *J. Phys. Chem.* **70**, 3293 (1966); on the rotation and vibration of HF in matrices (see *11*), M. T. Bowers, G. I. Kerley, W. H. Flygare, *J. Chem. Phys.* **45**, 3399 (1966). More recent unpublished calculations of Carlson and Moser indicate that CrO probably has a $^5\Pi(\delta^2\pi\sigma)$ ground state rather than that given in Table 3 or referred to in *29*.