Chem. Rev. **1996,** *96,* 2113−2134

New Developments in Matrix Isolation Spectroscopy

Vladimir E. Bondybey,* Alice M. Smith, and Jürgen Agreiter

Institut für Physikalische und Theoretische Chemie, Technische Universität München, Lichtenbergstrasse 4, D-85748 Garching, Germany

Received March 28, 1996 (Revised Manuscript Received July 16, 1996)

Contents

I. Introduction

The origins of matrix isolation spectroscopy can be traced to the early experiments of Vegard, beginning in the early 1920s.[1] Vegard bombarded condensed rare gases or nitrogen with electrons and observed the resulting luminescence. He noted the similarity between a persistent green ≈5577 Å luminescence emanating from the cryogenic solids, and the prominent line detected in aurora borealis, and saw in the low-temperature spectroscopy a convenient method to study auroral glow and other atmospheric phenomena. The line, originally assigned by Vegard to nitrogen atoms is now known to be due to the orbitally forbidden $^1S-^1D$ transition of atomic oxygen. The term "matrix isolation" was coined some 30 years later in 1954 by Pimentel and co-workers,[2] who used the technique for systematic studies of free radicals and other unstable or transient species.

Some 10 years ago, the emergence of alternative techniques for studying low temperature spectra, and in particular the development of supersonic jets seemed to spell doom to matrix isolation spectroscopy, or at least to limit considerably its usefulness. Combined with laser vaporization, electric discharges, or other methods for producing reactive intermediates, the collision-free environment of supersonic jets provided a convenient means for studying unstable species in the gas phase. In addition, supersonic jet spectroscopy had the great advantage of yielding the information contained in the rotational structure, which is lost in the nonrotating molecules in the solid matrix, and was free of other problems associated with "matrix effects" and perturbations of the molecular or atomic spectra due to interactions with the solid medium.

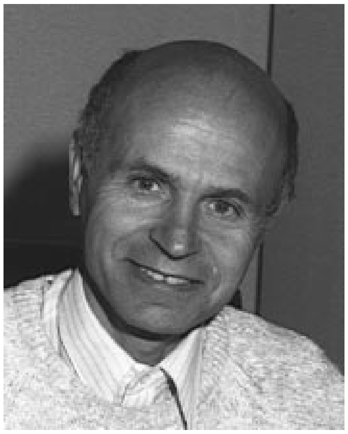
In spite of that, the steady flow of interesting matrix isolation studies continued, and the interest in the technique is on the rise, as evidenced for instance by the increasing attendance at the International Conferences on Matrix Isolation Spectroscopy. There are several reasons why, in spite of some disadvantages, matrix isolation remains a viable, useful technique.

In the first place, gas-phase studies of unknown spectra often represent a tedious, multidimensional search. The molecules must be studied "on the fly", in a given pulse, which either requires a very sensitive detection method (e.g. laser-induced fluorescence), or the ability to produce the species of interest in very high concentrations. In the matrix, on the other hand, the species can be accumulated over many minutes or even hours and can then be studied at leisure. By using absorption spectroscopy, a broad spectral range from the infrared far into the UV can be explored in a single experiment. Absorptions detected in such an experiment can be further investigated by, for instance, laser-induced fluorescence (LIF). If so desired, the spectral information obtained from the matrix studies can then form the basis for future detailed, high-resolution gas-phase studies, and the need for a tedious search of wide spectral regions can be avoided.

In the second place, while levels accessible from the ground state by an allowed transition are easily studied in the gas phase, investigation of forbidden transitions presents a much greater challenge. Studies of nonradiative processes occurring in the solid matrix[3] have shown that electronic relaxation often proceeds via a complicated interelectronic cascade involving two or more electronic states.[4] In the matrix, one can take advantage of our understanding of the relaxation pathways and mechanisms. By exciting higher-lying levels, the "forbidden" state can be populated by the nonradiative relaxation process and studied spectroscopically. It may be noted that also the selection rules are often relaxed in the matrix, making it possible to study directly processes rigorously forbidden in the gas phase.

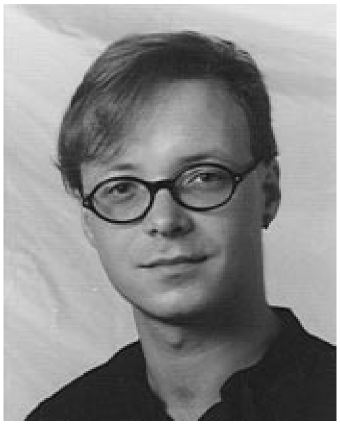
In the third place, matrix-isolated molecules can be viewed as simplest "solutions". Since many industrially important reactions occur in solutions, and the solvent can critically affect not only the rate, but even the outcome of chemical reactions, the solute−

S0009-2665(94)00262-1 CCC: $25.00



Prof. Dr. Vladimir E. Bondybey was born in Prague, Czechoslovakia, in 1940. He was educated at the Charles University, Prague, the University of Rostock, and the University of California, Berkeley, where he received his Ph.D. in chemistry in 1972 in the group of G. C. Pimentel. From 1973 to 1986 he was a distinguished member of the technical staff at AT & T Bell Laboratories. During the period 1987–1990, he was a full professor of chemistry at The Ohio State University. Since 1988, he has also been a full professor of physical chemistry at the Technical University of Munich. He is author of some 250 publications and has held about 170 invited talks at United States and international conferences.

Dr. Alice M. Smith was born in Willard, OH, in 1961. She received a B.A. in 1983 from Oberlin College graduating with highest honors in chemistry. For graduate studies in physical chemistry, she attended Caltech (1983–1984) and Harvard (1984–1988), with the support of a National Science Foundation (NSF) Predoctoral Fellowship. For her Ph.D. research she worked in the group of W. Klemperer on high-resolution laser photoacoustic and multipass absorption spectroscopies, receiving a Ph.D. in Chemical Physics in 1988 from Harvard University. As an Alexander von Humboldt and NSF–NATO Postdoctoral Fellow, she worked from 1989 to 1991 in the group of E. W. Schlag at the Technical University of Munich on the high-resolution UV spectroscopy of large molecules and molecular complexes. From 1992 to the present, she has been carrying out research with V. E. Bondybey on the Fourier-transform absorption and emission spectroscopies and laser spectroscopy of matrix-isolated transients toward completion of her German habilitation thesis. She is author of some 30 publications on molecular spectroscopy.



Jürgen Agreiter was born in München, Germany, in 1965. He received his diploma in physics in 1993 from the Technische Universität München. Since 1992, he has been working in the research group of V. E. Bondybey at the Institut für Physikalische und Theoretische Chemie, TU München. The major subject of his doctoral research (expected graduation by the end of 1996) is laser-induced fluorescence of matrix-isolated radicals, particularly molecular cations.

solvent interactions, the structure of solutions, and the dynamics of molecular solvation are problems of considerable current interest. Matrix-isolated atoms or molecules thus provide simple prototype systems for studying such interactions. There is thus a shift in emphasis, and the matrix effects, which were previously viewed as undesired disadvantages of the matrix techniques, become often the main focus of study. The gas-phase jet studies make it possible to determine with high precision binary interaction potentials.[5,6] The knowledge of the gas-phase potential between the solute—atomic or molecular—and the solvent, for instance rare gas atom, can then be used to interpret and understand the spectra of the solute in the rare gas solvent.[7,8]

There is a number of previous reviews of matrix isolation.[9,10] The purpose of the present article is therefore not a comprehensive review of the entire field. We will attempt to review selectively some of the advances in the field in the last 5−10 years. Of necessity, this review will not be exhaustive, but selective, and will emphasize more heavily work closer to the areas of interest of our research group. If we exemplify our presentation and discussion of some of these advances by studies originating in our laboratory, this is mainly because they are the examples with which we are most familiar.

Laser vaporization is one new technique whose introduction significantly facilitated the production of radicals, ions, and other reactive intermediates.[11−13] This method, which proved extremely useful for gas-phase jet studies, is undoubtedly at least equally promising in conjunction with low-temperature matrix studies. It was first used with laser-induced fluorescence,[13] but has now proved useful in combination with optical absorption, ESR, or infrared absorption spectroscopy as well. Unlike, for instance, vaporizing the samples in ovens or furnaces of various designs, with the laser techniques only a small amount of the material to be vaporized is directly heated, thus minimizing the danger of introducing impurities into the matrix sample. Applications of this technique will be one of the topics of this article.

Early matrix-isolation studies were mainly centered around neutral species, because it was widely believed that molecular ion spectra would be strongly perturbed and broadened due to the stronger interactions with the host. Later studies have shown that with a suitable choice of host matrix, relatively well resolved and unperturbed spectra of ions can be obtained.[14] Since one of the major prerequisites is that the ionization potential of the host is considerably higher than the electron affinity of the ion in the state to be studied, neon proved to be in most instances the most suitable medium. The recent studies in this area will be one of the topics of this review.

One of the problems of matrix-isolation spectroscopy lies in the unambiguous identification of the observed spectral features. In studies with the highly sensitive laser-induced fluorescence technique, for instance, a minor impurity exhibiting a high fluorescence quantum yield may often completely dominate the spectrum. In the absence of the information available in the high-resolution gas-phase rotational structure, the association of a spectrum with a particular carrier in matrices often containing a large number of species and fragments is often quite difficult. A seemingly obvious solution is deposition of mass-selected species. Several experimental difficulties however stand in the way of implementing this simple idea. In the first place relatively intense mass-selected ion beams have to be generated in order to obtain detectable amounts of the species to be studied. A second problem involves the deceleration of the ion beam prior to deposition. Species deposited with many electronvolts of energy can fragment on impact or penetrate deep into the weakly bound host solid, leading to guest−guest reactions or clustering. In spite of these difficulties, there has been considerable progress in this area in the last several years. The present review focuses on some of these recent developments.

II. The Use of Laser Vaporization in Matrix-Isolation Spectroscopy

A. Laser Vaporization and Its Advantages

Shortly after the invention of the laser in 1960, the plasma produced by focusing a laser beam on a solid target became a interesting point of study. The spectrum of this plasma was recorded, and by 1966 it was recognized that the sharp emission lines in the vacuum ultraviolet are due to emission lines of highly ionized atoms of the solid.[11] In 1969, the idea of chemical synthesis through laser vaporization was introduced. Schaeffer and Pearson showed that C_2 produced by YAG laser vaporization of carbon reacted with H_2 to yield acetylene, and laser-vaporized boron reacted with HCl to give BCl_3.[15] In the mid 1970s, Koerner von Gustorf et al. used laser vaporization to produce "naked" metal atoms for organometallic synthesis, whereby they cocondensed the evaporated metal with organic substrates at liquid N_2 temperatures.[16] The use of laser vaporization for the spectroscopy of reactive intermediates was pioneered in the late 1970s and early 1980s at Bell Labs. By employing a cold carrier gas to cool and quench the vaporization products, and laser-induced fluorescence to detect them, within a remarkably short time numerous molecular species (Pb_2,[13,17] Sn_2,[18,19] SiC_2,[20] Se_2,[21] SnBi,[22] Cr_2,[23] Cu_2,[24] and Be_2[25,26] were observed in the gas phase and spectroscopically characterized. At about the same time, the group of Smalley reported time-of-flight mass spectra of Al clusters produced by laser vaporization.[12] By the mid-1980s, the technique was established as generally useful in the generation of transients involving metals, alloys, and semiconductor molecules and clusters, and its use in a variety of fields continues to grow today. The products of laser vaporization need not be studied immediately in the gas phase, but can be trapped for leisurely investigation in suitable low temperature matrices.[20] Here we wish to concentrate particularly on the application of laser vaporization to matrix spectroscopy and discuss first its general advantages. Subsequently we will describe the specific implementation of the technique in our laboratory, and in the following sections then review and summarize some of the recent results obtained with the help of laser vaporization.

The laser vaporization production of transients has proven to be a highly versatile approach. Besides the fact that any solid or mixture of solids, including the most refractory materials such as tungsten or carbon can be vaporized, by simply adding a small amount of a suitable reactive gas to the inert carrier, the atoms or clusters produced by the laser vaporization can then further react to form an almost infinite variety of reaction products. By using such "reactive laser vaporization", for instance, a number of oxides, nitrides, hydrides, halides, carbides, and similar species can be generated.

A major advantage in contrast with thermal vaporization techniques where also the furnace or oven containing the sample, or at least the entire sample itself, has to be maintained for an extended period of time at high temperature, is that in laser vaporization in each laser pulse only a minute amount of the sample is instantaneously heated to a very high temperature and vaporized. This avoids the problems of sample contamination due to impurity vaporization or surface reactions or material segregation.

Besides neutral species, laser vaporization also produces electrons and abundant ions. We have demonstrated some time ago that in plasmas produced by vaporization of metals such as magnesium or calcium, often more than 10% of the atoms are ionized.[27] The laser vaporization can thus also be used as an efficient source of ions. By using organic precursor reactants, the laser-generated plasma can be used as a direct source of organic or organometallic species. Reactions of volatile organic compounds with the laser-produced plasma can result in their fragmentation, ionization, and charge-transfer reactions. We have in fact recently demonstrated that, for instance, reacting C_4N_2 diluted in the neon matrix gas with the plasma generated by vaporizing various metals proved to be a most efficient source of the $C_4N_2^+$ cation.

L. Knight and co-workers have shown in a series of elegant studies that with increased laser energy levels and tighter focusing, sufficient concentrations of not only neutral radicals, but also of cationic or anionic species in rare gas matrices can be generated for ESR detection. Since these ions are produced in the gas phase rather than in situ, their production can be monitored in real time rather than relying on matrix absorption after completed deposition. By mounting a quadrupole mass spectrometer in the line of sight of the metal surface just behind the matrix deposition surface they were able to monitor and optimize the ion generation in real time.[28]

The laser vaporization technique is also a very thrifty means of studying metals or metal containing species since only very small amounts (typically less than 100 μg per hour) are consumed. In this way studies of pure isotopic samples become affordable, which is especially advantageous for heavy metals with a large number of naturally occurring isotopes. Examples where such isotopic studies were instrumental in permitting analysis of the spectra are the dimers Sn_2 or Pb_2.[17−19]

B. The Advantages of the Pulsed Jet Laser Vaporization Technique for Matrix Isolation Spectroscopy

While a variety of laser vaporization configurations for matrix isolation spectroscopy is possible, we will describe here the configuration currently employed in our laboratory and shown schematically in Figure 1a.[29,30] It differs from most other setups using pulsed laser vaporization and continuous deposition of matrix gas in that it combines pulsed laser vaporization with a pulsed supersonic jet, whereby the matrix gas serves as inert carrier gas. In our setup, the sample in the form of a rotating disk is placed tangentially to the matrix gas flow channel. We use the pellet form rather than the rotating rod configuration originally used by Leach and co-workers[11] because it offers more versatility. While not all samples are readily available in rod form, almost any substance can be obtained as a powder and pressed into a flat pellet. Thus almost any solid sample or mixture can be vaporized using several millijoules of frequency-doubled Nd-Yag laser light. The laser pulse is synchronized with the opening of a pulsed valve, so that the plasma is cooled and swept by the neon carrier gas flowing through the channel. About 30 mm downstream from the opening of the expansion channel, the neon carrier gas with the products of laser vaporization are frozen onto the cooled substrate. The modular design of our cryostat and vacuum systems allows considerable flexibility of our experiments with the possibility of an easy interchange of the laser vaporization source with for instance our self-igniting electric discharge[31] or other types of sources. Alongside the matrix experiments, the same source can be used in complementary gas-phase experiments, employing laser-induced fluorescence or mass spectrometric detection.

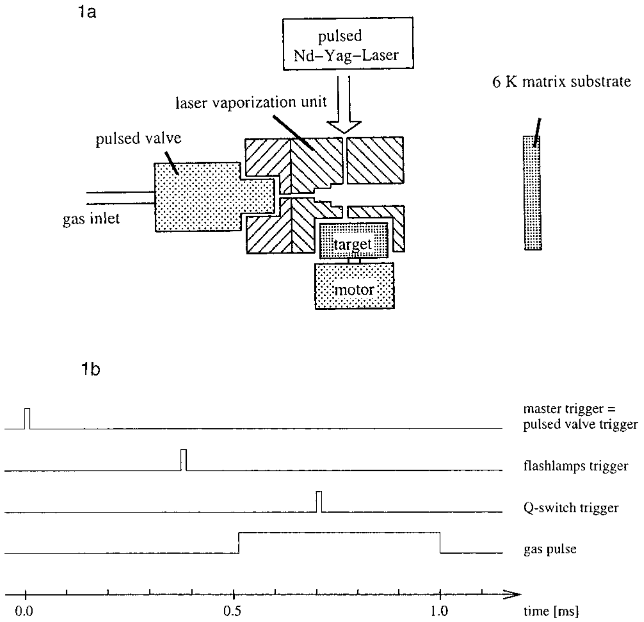


Figure 1. (a) Schematic of our laser vaporization source of matrix-isolated transients, consisting of a pulsed gas valve (inlet for matrix gas and potential gaseous precursor) and a fixture containing the pressed pellet to be vaporized. A gas pulse streams over the rotating target just as it is struck with the doubled light of a pulsed Nd-Yag laser. The hot species are cooled in the adiabatic expansion before deposition on the 6 K surface. (b) Schematic of the synchronization of the gas pulse and laser pulse leading to the optimal production of small transient species, and avoidance of a strong layering of the matrix.

The use of our pulsed jet/pulsed laser vaporization source has numerous additional advantages. Combining pulsed laser vaporization with the conventional continuous spray matrix gas deposition necessarily leads to strong layering of the vaporization products in the matrix which may be undesirable. This layering is avoided or at least minimized in the pulsed source, where synchronizing laser pulses with narrow bursts of the matrix gas (see Figure 1b) results in a much more uniform distribution of the products in the matrix.

In addition, as we have recently discussed elsewhere, the pulsed jet deposition has a number of other advantages independent of laser vaporization. Deposition of small bursts of the matrix gas results in greatly improved optical quality of the matrix samples (ref 32 and references therein). Unlike the conventional continuous deposition which often results in highly scattering samples, the pulsed method leads to almost perfectly clear, well-annealed matrices, and this greatly facilitates spectroscopic studies.

The laser-induced plasma is extremely hot, with temperatures high above the boiling point of the sample, typically around 10^4 K, and with particle velocities exceeding 10^4 m/s.[33,34] The impact of such high-energy atoms, electrons, or ions could lead to reactions on or near the matrix surface and also cause considerable damage to the crystal lattice, leading to broadened and perturbed spectra. Thus for instance in optical absorption spectra of mass-selected ions landed with residual kinetic energies of about 50 eV, all the absorption peaks exhibited widths of some 100−150 cm^{-1}. The spectra of the same species deposited by our pulsed techniques exhibited discrete and very sharp (< 2 cm^{-1} wide) site structure.[31] In the high-pressure carrier gas present in the flow channel the initially present "hot" species in the plasma are cooled to ambient temperatures prior to exiting the flow channel and thus the matrix surface is protected from the impact of high-energy particles.

This adiabatic expansion of the gas exiting the flow channel can in itself be useful. It results in further reducing the translational temperature, and cools the internal modes of the products. Besides being useful in most gas-phase experiments for reducing the rotational temperatures and Doppler line widths, it can also significantly enhance cluster formation. Such clustering can be optimized through a suitable choice of experimental conditions and flow channel geometry. If desired, matrices greatly enriched in dimer and cluster concentrations can be generated.[35]

C. Examples of Recent Use of Laser Vaporization in Matrix Isolation Spectroscopy

1. Electron Spin Resonance

The laser vaporization technique has greatly extended the variety of chemical systems that can be studied by rare gas matrix isolation electron spin

Table 1. A Noncomprehensive List of Neutral and Ionic Radicals Recently (1989 to Present) Studied by the Application of Laser Vaporization (LV) or Reactive Laser Vaporization (RLV) to Matrix-Isolation Spectroscopy

generation	spectroscopy	species
		Neutral Radicals
LV	ESR	Gd_2,[204] (Co_3, Rh_3, Ir_3)[35] (B_3, Al_3),[67] Mn_2,[134] Cu_7[69]
	IR	Si_n ($n = 3, 4, 6, 7$),[70] Se_n ($n = 2-4$)[205]
	magneto-IR	(Si_2, Ge_2, Sn_2),[65] (Se_2, Te_2)[206]
	Raman	(Si_4, Si_6, Si_7)[71]
RLV		
solid−solid	ESR	(AlC, AlC_2),[207] (SiB, SiA),[41] (PdB, PdAl),[208] BNB,[42] (TiNb, ZrNb, ZrV, HfV),[209] Ga_2As_3,[68] CrMn,[134] (XCu, XAg, XAu, X = Mo, W),[210] ScCr[211]
solid−gas		(CoX_2, RhX_2, IrX_2; X = H,[212] X = O[213]), BCO,[214] (BNH,BO),[215] (VH_2, NbH_4, TaH_4),[216] $PdCH_3$,[217] $CuCH_2$,[131] (PO_2, AsO_2),[218] HAlOH[219]
solid−solid	IR	(GeSi, SnSi),[220] (GaP, GaAs, GaSb),[221] (InP, InAs, InSb),[222] BC_2,[223] (AlC, Al_2C, Al_2C_2)[224]
solid−gas		BCO,[214] NbH_2,[216] B + X (see text), Be + X; X = CO,[225] N_2,[226] CO_2,[227] O_2,[228] H_2,[229] FeH_n ($n = 1-3$),[230] (ZrHn, HfHn; $n = 1-4$),[45] (ZnH_2, CdH_2),[46] TiH_n ($n = 1-4$),[224] AlC_2H[224]
solid−solid	Magneto-IR	TeSe[206]
solid−solid	LIF	BN,[29] BC[30]
		Ionic Radicals
LV	ESR	Nb_2^+,[136,a] (Co_2^+, Rh_2^+, Ir_2^+),[135] (Cu_2^+, Ag_2^+, Au_2^+),[133] Mn_2^+,[134] Mg_n^+, $n = 1-6$,[231] Sc_2^+,[219] (Si_2^+, Ge_2^+)[129]
RLV	ESR	(ZrO^+, HfO^+),[136] (YB^+, YAl^+),[232] ($GaAs^+$, GaP^+),[131] PdH_2^+ [233]

[a] According to the work of James and Sinard[234,235] Nb_2^+ might be symmetrical Nb_2O^+.

resonance spectroscopy, as discussed in detail by Knight[36] and exemplified in Table 1. Even in ESR, where only open-shell species are detected, the assignment without mass selection often represents a major hurdle. A nice example demonstrating this point is AlF^+.[37] Conventional vaporization of the AlF_3 (s) and Al (s) mixture from a tantalum oven and the deposition of the reaction products with simultaneous ionization by neon resonance radiation (16.8 eV) resulted in an ESR spectrum consisting of a sextet of doublets, as expected for the AlF^+ cation. However, discrepancies between the observed and calculated Al hyperfine structures prompted further investigations. When AlF^+ was generated by reactive laser vaporization with photoionization as above, a different spectrum in excellent agreement with theory was detected. The spectrum observed in the thermal vaporization was most likely due to the “contaminant” $AlOF^+$. Since ^{16}O has $I = 0$, its presence would not be obvious from the hyperfine structure. It should be possible to test this in a ^{17}O isotopic experiment (^{17}O has $I = ^5/_2$). While incorporation of the rare isotope in a conventional oven experiment would be difficult, it is easy to introduce a small amount of $^{17}O_2$ gas in a laser vaporization experiment.

This ability of reactive laser vaporization to work with minute amounts of rare isotopic samples was for instance put to good use in the electronic characterization of the singly occupied MO of a variety of metal monoxides. By using isotopically enriched ^{17}O samples, information about the hyperfine splitting constants and the distribution of the unpaired electron in, e.g. the group III oxides AlO, GaO, and InO, as well as ScO and YO, could be obtained.[36]

Another area nicely illustrating the utility of laser vaporization is the chemistry of boron. Conventional vaporization of boron requires extremely high temperatures (above 2550 °C) and is further complicated by the corrosive nature of the molten element. Laser vaporization of solid boron, its compounds, or solid mixtures is, on the other hand, straightforward, and was used to trap simple boron compounds not only for ESR studies, but for IR and LIF investigations also. Knight and co-workers were the first to use this technique to characterize the ground states not only of the B atom[38] and B_2,[38] but also of BF^+,[39] BC,[40] SiB,[41] and BNB[42] molecules to name just a few. By vaporizing pressed mixtures of B/^{12}C and B/^{13}C they obtained the ESR spectra of the BC radical. These spectra yielded the first experimental evidence for the $^4\Sigma^-$ ground-state symmetry of BC, which could then be confirmed by laser-induced fluorescence studies (see the LIF section below).

2. Infrared and Optical Absorption

Matrix isolation as originally conceived in the laboratory of Pimentel was mainly used in conjunction with optical absorption spectroscopy. The highly versatile laser vaporization technique can be naturally employed for generation of samples for characterization by infrared or visible absorption spectra also, and numerous such studies have recently been reported. One difficulty of infrared studies lies in the unambiguous identification of the absorbing species. The complex reactions in the laser-produced plasma can lead to a large variety of products, and besides neutrals, ionic species can also be generated. Since traces of water or other atmospheric components are difficult to eliminate completely, undesired products due to reactions with these impurities can also appear. Isotopic studies, if necessary with isotopically enriched samples, are the most important assignment tool, and as previously noted, such studies are much easier with the laser vaporization technique than with thermal vaporization. Comparison with state of the art theoretical predictions of not only vibrational frequencies, but also of relative band intensities can be extremely helpful. Nice examples of such a constructive interplay between experiment and theory is a series of recent studies of carbon and silicon-carbon clusters by Graham, Rittby, and coworkers.[43,44] They employ theoretical *ab initio* frequencies and intensities, as well as computed isotopic shifts as a tool in assigning the experimentally observed infrared absorption lines.

Laser vaporization was recently applied very successfully to a number of different systems by Andrews and co-workers. See Table 1. A series of infrared studies of this group involved reactions of laser-vaporized metal atoms with hydrogen (H_2, HD, and D_2). They carried out a comparative study of the group IVA metal hydrides—TiH_4, ZrH_4, and HfH_4, the latter two observed for the first time. The observation of a higher asymmetric stretching fundamental for HfH_4 than for the lighter ZrH_4[45] molecule was attributed to relativistic effects in the heavier metal. A similar study of the group IIB metal hydrides—Zn, Cd, and Hg—has also been recently reported.[46]

As noted above, the advantages of laser vaporization are particularly important for highly refractory elements such as boron, and the chemistry of boron compounds was another area extensively studied by the Andrews group. In a long series of studies, they have vaporized boron, and reacted the laser-produced plasma with a variety of gaseous elements or compounds to produce numerous novel boron compounds. Among the reactants studied were for instance H_2,[47] O_2,[48] N_2,[49] CO,[50] halogens,[51] H_2O,[52] CO_2,[53] CS_2,[54] CH_4,[55−57] C_2H_2,[58,59] NH_3,[60,61] and SO_2.[62] The reaction products were in each case trapped in argon matrices, and their infrared spectra were investigated. Numerous polyatomic products were identified for the first time. The assignments were in many cases made in cooperation with the theorists J. M. L. Martin and P. R. Taylor or R. J. Bartlett.

One interesting example is the BN analogue of acetylene. Andrews et al. were able to produce HBNH efficiently by the reaction of laser-produced boron atoms with ammonia gas, in high enough yields to obtain good quality infrared spectra as shown in Figure 2.[60,61]

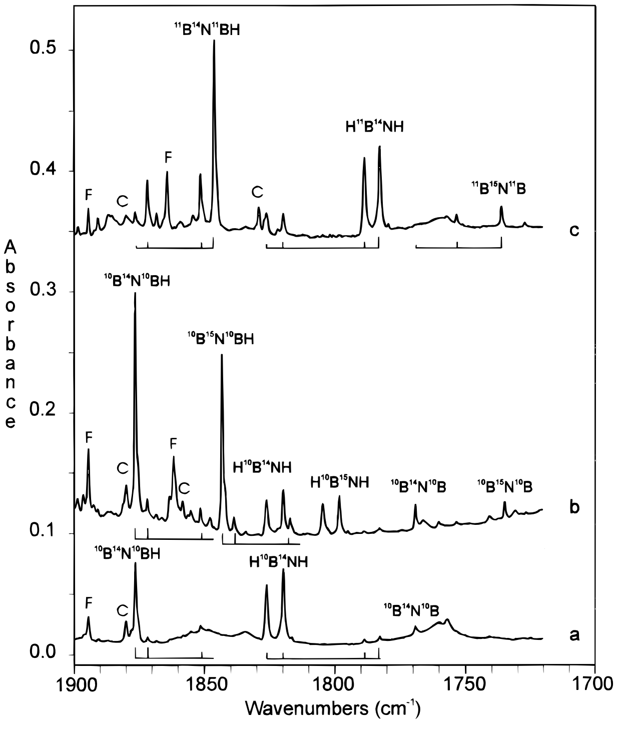


Figure 2. Infrared spectra in the B−N stretching region 1900−1725 cm^{-1} for pulsed-laser ablated boron atom−ammonia−argon samples condensed at 10 ± 1 K: (a) ^{10}B + $^{14}NH_3$, (b) ^{10}B + $^{14}NH_3/^{15}NH_3$, and (c) ^{n}B + $^{14}NH_3$. Horizontal lines indicate boron isotopic multiplets (including site splittings for HBNH). From C. A. Thompson and L. Andrews: *J. Am. Chem. Soc.* **1995**, *117*, 10125.

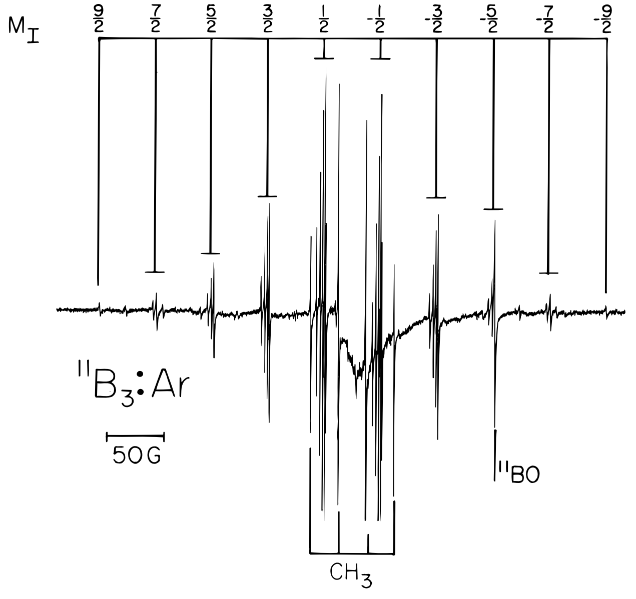


Figure 3. Electron spin resonance (ESR) spectrum of the $^{11}B_3$ molecule isolated in an argon matrix at 4 K. The center of the spectrum is at $g = 2.0$ and $\nu = 9.5576$ GHz. Since the ^{11}B nucleus has $i = {}^{3}/_{2}$, the 10 groups of lines demonstrate the equivalency of the three boron atoms in the trimer. (CH_3 and ^{11}BO radical impurities are indicated.) From Y. M. Hamrick, R. J. Van Zee, and W. Weltner, Jr.: *J. Chem. Phys.* **1991**, *95*, 3009.

Another group very active in laser vaporization matrix isolation experiments, beginning with their interest in carbon cluster molecules,[63] is that of Weltner and Van Zee. Part of their recent work has been summarized.[64] See also Table 1. In addition to carrying out conventional ESR and IR experiments, they have recently combined Fourier-transform IR absorption with Zeeman spectroscopy to study magnetic molecules produced by laser vaporization. This allows the direct measurement of the zero-field splitting parameters in triplet and higher spin molecules that are not detectable by conventional ESR. These additional (magnetic-dipole) transitions, generally occurring weakly in the far-infrared, but for large spin−orbit coupling (i.e. heavy atoms) more intensely in the midinfrared, can be discriminated from the usual vibrational spectra by measurements in a magnetic field where Zeeman splittings cause broadening. Allowed transitions to very low-lying states may also be observable in this region. For example, their magneto-infrared spectra of the group IV diatomics, Si_2, Ge_2, and Sn_2 revealed the lowest ${}^3\Pi_u \leftarrow X^3\Sigma_g^-$ electronic transitions of these diatomics in the infrared. In each case, several vibronic bands, each split into Ω triplets in the upper state, were observed. A Zeeman effect on these lines detected in magnetic fields up to 4 T verified their assignment, without the need for isotopic enrichment studies. For the heavier Sn_2 molecule, two additional transitions, the $1_u \leftarrow X0_g^+$ ($\nu_{00} \cong 1800$ cm^{-1}) and a magnetic dipole transition, $1_g \leftarrow X0_g^+$ at 770.5 cm^{-1}, were observed.[65]

Another area into which this group has ventured is the ESR and IR measurements of larger semiconductor and metallic clusters, e.g. ESR on trimers such as B_3 (Figure 3) or Al_3,[66,67] or on larger clusters such as Ga_2As_3[68] or Cu_7.[69] (See Table 1.) In order to produce these larger clusters more efficiently, they employ a "high-pressure" deposition (10^{-3} -10^{-4} mbar near the matrix substrate), allowing the laser vaporized species to aggregate before condensation by doubling the normal rare gas flow. An open-cycle cryostat reaching temperatures down to 2.5 K toler-

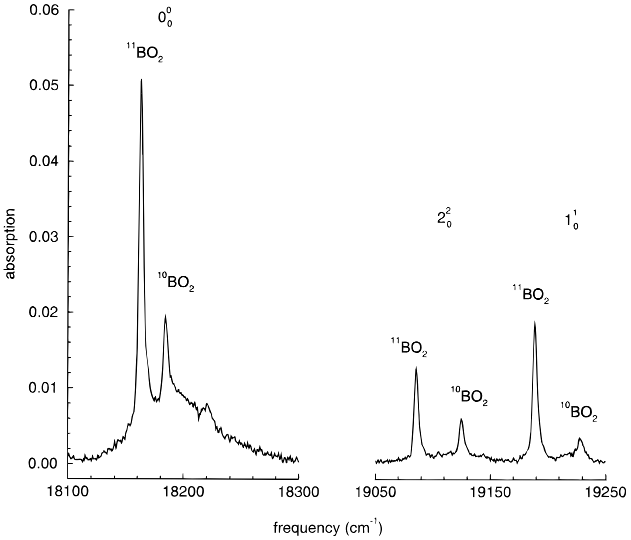


Figure 4. Parts of our Fourier-transform visible absorption spectrum showing the $A^2\Pi_u \leftarrow X^2\Pi_g$ transition of BO_2 in a neon matrix at 6 K. BO_2 was formed here through pulsed laser vaporization of boron solid, the oxide being formed as an "impurity" through reaction with residual oxygen. For further details, see ref 236.

ates these high pressures even for neon matrices. Two excellent experimental studies on silicon clusters produced by laser vaporization have recently appeared. Weltner's group reported the infrared spectra of Si_n, $n = 3, 4, 6, 7$, in neon, argon, and krypton matrices,[70] complementing the previous Raman studies of Si_n, $n = 4, 6, 7$ in N_2 matrices using mass-selection at Bell Labs.[71] These studies unanimously support the predicted 3D structures of Raghavachari.

Besides the traditional infrared region below 4000 cm^{-1}, studies in the near-infrared or visible regions, where in particular open-shell species such as molecular ions or radicals have strong transitions, can be also very useful. Of advantage are here not only the larger oscillator strengths of the electronic transitions, but also the easier identification of the carrier. Unlike the infrared region, where mostly only one, or at best a few bands are observed, the electronic transitions often consist of a regular pattern of vibronic bands, which may greatly facilitate unambiguous assignment. As an example, Figure 4 shows the visible absorption spectrum of BO_2 produced by laser vaporization of boron in the presence of traces of oxygen. Clearly visible is the tell-tale isotopic splitting of the individual vibronic bands, and in the regular pattern of absorption bands, all three vibrations in the excited A state of BO_2 can be detected.

One advantage of low-temperature solids is that many relaxation processes which proceed very rapidly at room temperature are greatly slowed down in low- temperature solids. If a molecule has a long-lived excited electronic state, and if there is an efficient way of populating it, it is also feasible to measure optical absorption spectra of electronically excited molecules. As an example, Figure 5 shows the infrared absorption spectrum of the C_3 molecule in its lowest triplet state. The carbon clusters including C_3 were generated by laser vaporization of graphite, and the long-lived state was populated by optical pumping. By comparing the infrared spectra with the pumping radiation on and off, the absorption bands due to the metastable excited molecule, which are only detected in the presence of the pump radiation, can easily be distinguished.

3. Laser-Induced Fluorescence

The most sensitive spectroscopic technique available for matrix studies is laser-induced fluorescence (LIF). While for infrared studies typically concentrations of the order of 1×10^{-3} are needed, LIF often permits detection of species in the 1×10^{-12} concentration range, and in favorable cases single molecules may be detected.[72,73] In the time since our first LIF spectroscopic studies of transients produced by laser

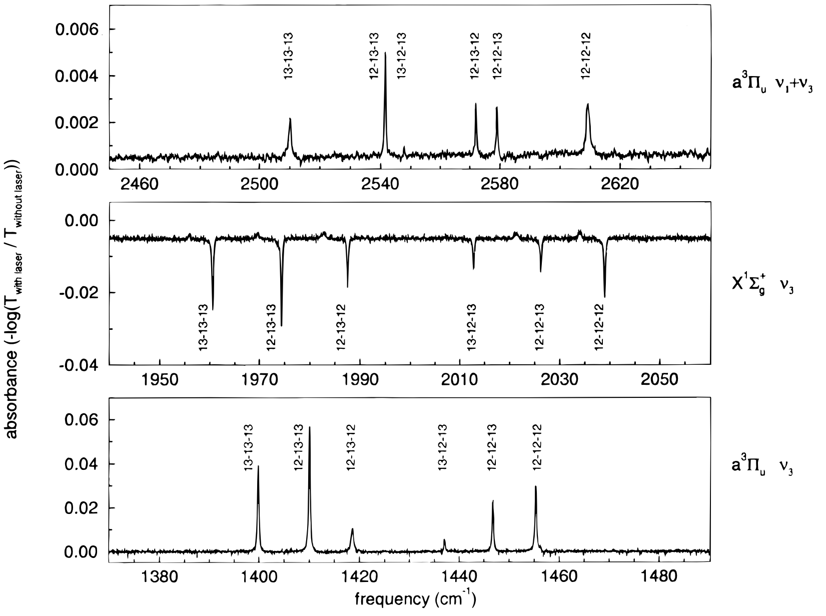


Figure 5. The Fourier-transform infrared difference spectrum illustrating the changes in the infrared spectrum resulting from laser pumping of the C_3s $A^1\Pi_u \leftarrow X^1\Sigma_g^+$ origin at 24369 cm^{-1} in an argon matrix. The six isotopomers of C_3 were formed from laser vaporization of a ^{12}C:^{13}C solid mixture. Lower and upper trace: New absorptions appear resulting from the ν_3 and $\nu_3 + \nu_1$, respectively, of the metastable a $^3\Pi_u$ state. Middle trace: At the same time, the ground electronic state is strongly depleted.

Table 2. Spectroscopic Constants of Electronic States of BN[a]

		experimental		theory		
state	constant	present	previous[b,c]	*d*	*e*	*f*
$X^3\Pi$	T_e	0.0	0.0	0.0	0.0	4.277
	w_e	1519.2	1514.6	1491	1508.2	1479
	w_ex_e	12.6	12.3	13	12.5	
$A^3\Sigma^+$	T_e	9777.6				10244
	w_e	1826.8				1783.6^g
	w_ex_e	14.2				
$B^3\Sigma^-$	T_e	10332.3				9578
	w_e	1074.8				1057.7^g
	w_ex_e	10.4				
$D^3\Pi$	T_e	27910.6	27875.0			27624
	w_e	1325	1317.5			1292.5^g
	w_ex_e	14.9^h	14.9			
$a^1\Sigma^+$	T_e	$15 < a < 182$		381 ± 100	190 ± 100	180 ± 110
	w_e	1700.9	1732^g	1686	1697.5	1674.6^g
	w_ex_e	9.9		11.3	11.2	
$b^1\Pi$	T_e	$a + 3646.1$	$a + 1830.97$			$a + 3633$
	w_e	1532.5	1658^g			1498.9^g
	w_ex_e	11.1				

[a] All values in cm^{-1}. [b] A. E. Douglas and G. Herzberg: *Can. J. Res. A* **1940**, *18*, 179. [c] H. Bredohl et al.: *J. Phys. B: At. Mol. Phys.* **1984**, *17*, 95. [d] J. M. L. Martin et al.: *J. Chem. Phys.* **1992**, *97*, 6549. [e] K. A. Peterson: *J. Chem. Phys.* **1995**, *102*, 262. [f] C. W. Bauschlicher, Jr. and H. Partridge. *Chem. Phys. Lett.* **1996**, *257*, 601. [g] Calculated from the theoretical $\Delta G_{1/2}$'s and our experimental w_ex_e's using the relation $\Delta G_{1/2} = w_e - 2w_ex_e$. [h] Fixed at gas-phase value.

vaporization, the technique has become well established for gas-phase work, and a number of studies from different groups has appeared. On the other hand, most matrix studies using this technique originate from our laboratory. We have been able to apply the matrix LIF studies combined with laser vaporization quite successfully to a variety of systems.

In our experiment, samples are studied spectroscopically either in emission or absorption using a Bruker HR-120 Fourier-transform (FT) spectrometer with a maximum resolution of 0.0015 cm^{-1}. With a suitable choice of broad-band source, beam splitter, and detector, absorption spectra from 500 to 30000 cm^{-1} are measured. The sample fluorescence is excited by tunable cw dye or titanium-sapphire lasers, all pumped by Ar ion lasers. The emission is focused on the entrance aperture of the FT spectrometer, and the signal is detected using a photomultiplier (11000–30000 cm^{-1}) or a liquid–nitrogen-cooled germanium detector (5500–12000 cm^{-1}).

Our recent LIF studies have also focused on the simple compounds of boron, and in particular on the BN[29] and BC[30] diatomics. The corresponding solids, boron nitride and boron carbide, are well-known materials with fascinating properties. They are among the hardest substances known to man, and also belong to the most refractory materials, which makes them particularly good candidates for laser vaporization studies. The outstanding properties of the B–C–N solids make them technologically interesting, and the possibilities of formation of thin films of these species by molecular beam epitaxy or chemical vapor deposition were the subject of numerous studies. In spite of the extensive interest in the materials, the information available even about the diatomic BN and BC precursor molecules was extremely fragmentary.

BC in neon matrix was first generated by laser vaporization by Knight, and its observed ESR spectrum[40] confirmed the previous theoretical predictions of a $^4\Sigma^-$ electronic ground state. However, even in the case of the ground state, no experimental information about the vibrational constants of BC was available. The isoelectronic C_2^+ ion in neon matrix was detected in 1987, and its $B^4\Sigma_u^- \leftrightarrow X^4\Sigma_g^-$ transition was observed. Maier et al. used in situ photolysis of chloroacetylene to generate the ion,[74] while in our laboratory laser vaporization of graphite[75] was employed, and it was characterized by its absorption and laser-induced fluorescence spectrum. The analogous transition of BC was observed in the gas phase a few years later.[76]

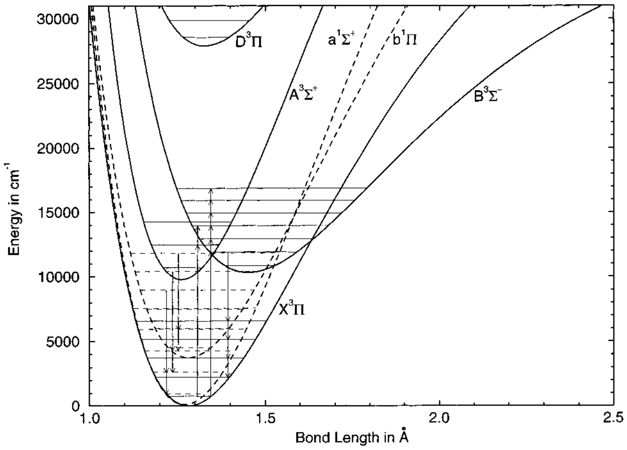


Figure 6. Potential energy surfaces of the low-lying states of ^{11}BN extracted from our LIF studies. The solid curves and lines belong to the triplet levels, and the dashed to the singlet levels. BN was formed through laser vaporization of a boron nitride pellet and isolated in solid neon at 6 K. Excitation of the $B^3\Sigma^- \leftarrow X^3\Pi$ and the $A^3\Sigma^+ \leftarrow X^3\Pi$ transitions (see Figure 7) led to $B^3\Sigma^- \rightarrow X^3\Pi$ and $b^1\Pi \rightarrow a^1\Sigma^+$ emission, as illustrated by the arrows.

Until our recent matrix studies, only the $D^3\Pi$–$X^3\Pi$ transition of BN in the near-ultraviolet (analog of the Swan bands of C_2) was known. It was observed through early gas phase work of Douglas and Herzberg,[77] and a 1970 matrix absorption study by Mosher and Frosch.[78] Also two weaker singlet transitions originally detected by Douglas & Herzberg were recently assigned,[79] but as our results below

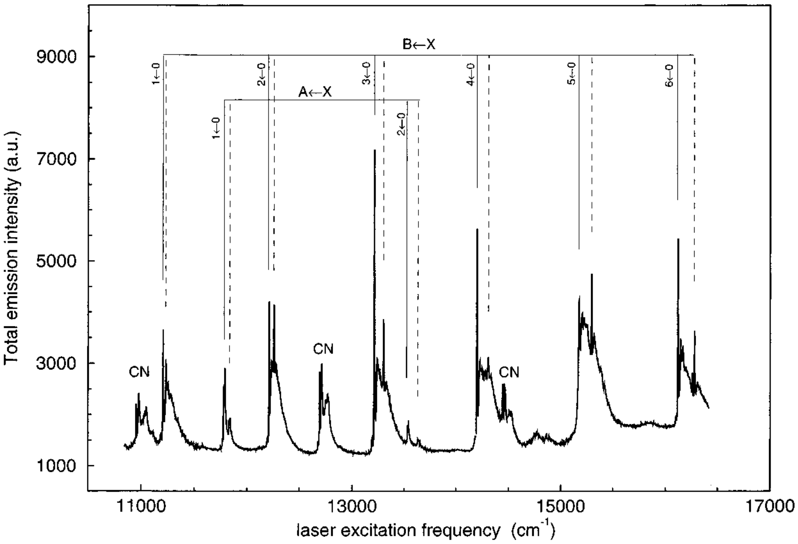


Figure 7. Laser excitation spectrum of the $B^3\Sigma^- \leftarrow X^3\Pi$ and the $A^3\Sigma^+ \leftarrow X^3\Pi$ absorptions of BN in solid neon taken over a 5000 cm^{-1} range, recorded through phase-sensitive detection of the total emission signal while scanning the amplitude-modulated cw dye laser. The vibronic transitions due to ^{11}BN are indicated by solid lines and those due to ^{10}BN by dashed lines. The CN radical is also formed, most likely through reaction with CO_2 impurity in the laser-induced plasma.

show, both assignments were in error. Very useful in analyzing and interpreting the results were, on the other hand recent high quality theoretical studies.[80,81]

We have now succeeded in producing both molecules and clarifying their electronic structure and spectroscopy. We vaporized pressed mixtures of boron and graphite powders to produce BC in a neon matrix, while BN was produced by vaporization of solid boron nitride. Both molecules were produced in sufficient concentrations for direct observation by electronic absorption spectroscopy. The molecules were then excited by cw laser radiation, and the emission analyzed in our FT-IR spectrometer.

One useful feature of matrix spectroscopy is the efficient nonradiative relaxation, which often proceeds by a cascade process involving several electronic states.[4] By taking advantage of such processes, we could in both molecules observe and characterize not only states with ground state multiplicity, but also states populated by intersystem crossing—that is singlet states of BN, and doublet states of BC.

This can be understood with the help of the BN potential energy diagram in Figure 6. At least three low-lying excited triplet states accessible from the $X^3\Pi$ ground state are expected, and all three are actually observed in absorption. The newly observed $A^3\Sigma^+$-$X^3\Pi$ and $B^3\Sigma^-$-$X^3\Pi$ absorptions are shown in Figure 7 through their laser excitation spectra in a neon matrix. Following laser excitation of these absorptions one observes not only fluorescence from various triplet vibrational levels into the ground state, but also, as shown in the diagram, intersystem crossing into the nearby $b^1\Pi$ state takes place, so that also extensive $b^1\Pi \rightarrow a^1\Sigma^+$ emission into the lowest singlet state is present. Since the ^{10}BN and ^{11}BN bands are clearly resolved and can be selectively excited, the vibrational numbering in all states can be unambiguously established. By careful analysis of the spectra and least-square fit of all the observed bands, we could derive molecular constants for all five low-lying states of BN, and these are listed in Table 2. One can note that even though $X^3\Pi$ is indeed the ground state of BN, the T_e of the $a^1\Sigma^+$ is less than 182 cm^{-1}, even lower than suggested by the two most recent ab initio calculations (see Table 2).

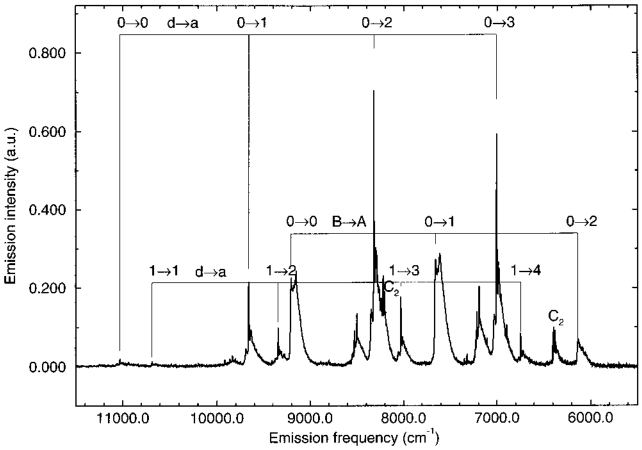


Figure 8. Fourier-transform near-infrared emission of ^{11}BC in solid neon produced through laser vaporization of a boron/graphite solid mixture. The origin of the $B^4\Sigma^- \leftarrow X\ ^4\Sigma^-$ absorption at 18010.4 cm^{-1} is excited and not only the emission to the ground (not shown) and $A^4\Pi$ observed, but through an effficient nonradiative relaxation process, low-lying doublet levels are populated and two progressions of the $d^2\Sigma^+ \rightarrow a^2\Pi$ emission observed.

Quite analogous is our study of BC. The samples produced by vaporization of a pellet of a mixture of boron and graphite powders exhibited the known $B^4\Sigma^-$- $X^4\Sigma^-$ absorptions. The emission resulting from selective resonant excitation of these absorptions exhibited not only emission from the B state back into the ground state, but also into the predicted lower lying $A^4\Pi$ state. Similar to BN, intersystem crossing populated also the doublet manifold, and fluorescence between two new electronic states, $d^2\Sigma^+$ and $a^2\Pi$, previously unknown experimentally, but predicted by the thorough theoretical calculations of Hirsch and Buenker[82] was observed (See Figure 8). From these spectra, the spectroscopic constants for five low-lying electronic states of BC shown in Table 3 could be

Table 3. Spectroscopic Constants of Electronic States of BC[a]

	present experiments			previous theory[b]		
state	T_e	w_e	w_ex_e	T_e	w_e	w_ex_e
$X^4\Sigma^-$	0.0	1172.6	10.3	0.0	1140	8.5
$A^4\Pi$	8604.5	1574.8	13.9	9270	1550	13.0
$B^4\Sigma^-$	17951.8	1289.6	8.5[c]	17900	1250	8.5
$a^2\Pi$	a	1394.5	13.5	4600	1350	30
$d^2\Sigma^+$	$a + 11210.3$	1031.1	4.5[c]	13300	1100	4.5
$e^2\Pi$				16690	780	

[a] All values in cm^{-1}. [b] G. Hirsch and R. J. Buenker: *J. Chem. Phys.* **1987**, *87*, 6004. [c] Fixed at theoretical value.

derived, in most cases in good agreement with the theoretical predictions.

III. Quantum Hosts

An interesting and expanding area of research involves studies in very light and weakly bound condensed systems, such as solid hydrogen or liquid or solid helium. Such “quantum materials” exhibit large amplitude zero-point motion of their atoms or molecules from their idealized lattice positions. The zero-point motion is not negligible compared to the nearest neighbor distances, and the importance of quantum effects is greatly increased.[83]

Helium, the lightest and most inert of the rare gases is such a quantum material with remarkable properties. Interesting is the availability of two isotopes with markedly different properties, ^{3}He and ^{4}He. Both elements have two liquid phases, with ^{4}He-II being superfluid below $T_\lambda = 2.174$ K. A quite unusual property of ^{3}He is that it melts exothermically. ^{4}He can under ambient pressure not be solidified, but numerous studies of “isolated” species have been performed in the liquid, both above and below the superfluid transition (λ point). Gas-phase metal ions produced by laser ablation can be accelerated toward the helium bath and if desired neutralized in the liquid for instance by electrons produced by a field emission tip. A group at the University of Heidelberg has in this manner studied recombination light emission as well as laser-induced fluorescence from the neutral atoms.[84]

The implantation of atoms or ions can be even more easily accomplished by placing the laser vaporization target directly in the liquid helium, thus circumventing the problem of the repulsive potential at the liquid surface.[85,86] By placing the helium and the target in a high-pressure cell, studies in solid helium are also possible. In this manner, Hänsch and coworkers were able to study the effect of the liquid–solid phase transition on the spectra of e.g. Ba or Cs atom “defects” in helium. The authors observed only insignificant changes in the LIF and interpreted this in terms of incorporation of the foreign atoms in nanometer-sized bubbles or cavities, rather than as interstitial or substitutional impurities in the solid lattice as in other rare gas matrices.[87] With this “bubble” model they were able to reproduce qualitatively the features of the observed spectra; a large blue shift, asymmetry and broadening (~10 nm) of the excitation lines, and a smaller shift and broadening of the emission. It may be noted that the same “bubble” model was a number of years ago employed to explain the spectral properties of Rydberg states of e.g. NO in conventional matrices (Ne, Ar, Kr, Xe).[88−90] The alkali metals in particular, and to some extent also the earth alkali metals, have partially a “Rydberg” character, with a loosely bound electron, and a closed rare gas electron shell underneath. A comparison with the atomic spectra of other elements, e.g. transition metals, would be interesting.

Of interest in this connection is also our recent study of Tl atoms. We have investigated the 7s $^2S_{1/2} \leftarrow$ 6p $^2P_{1/2}$ transition of thallium both in binary Tl–Rg complexes[6] and in rare gas solids.[8] While the atomic transition is strongly red shifted in the binary complexes, with the shift increasing from Ar to Xe, it undergoes large blue shifts in the solid matrices, which decrease from Ar to Xe. We have interpreted the observed shifts and spectral lineshapes with a model, where the excited, Rydberg-like state of thallium rather than forming a “bubble” around it, resembles more a Tl$^+$ ion, with the electron being delocalized into the lattice.

A related interesting area involves studies in helium clusters. While $^4He_2$ is only marginally bound (and $^3He_2$ not at all),[92] supersonic expansion of a high pressure (≈80 bar) helium gas from a cooled (10−25 K) source can produce large helium “droplets” or clusters with temperature of about 0.4 K and containing typically 10^3−10^4 atoms.[93] Using for instance a pick-up arrangement, various “impurity” atoms or molecules can be incorporated in the cluster and studied spectroscopically. Pioneering studies of this type on helium clusters originate from the laboratory of P. Toennies in Göttingen,[94,95] and from the group of G. Scoles at Princeton.[96] By monitoring the depletion of signal due to tunable infrared diode laser coaxial with the cluster beam, the Göttingen group was able to measure the infrared absorption spectra of several molecular impurities including SF_6.[97−99] The spectra of SF_6 exhibited an interesting spectral profile reminiscent of a gas-phase vibrational band with central Q-branch redshifted by 1.415(1) cm^{-1} from its gas-phase frequency and a partially resolved rotational structure, as shown in Figure 9a. However, to fit satisfactorily the observed structure, an effective rotational constant about a factor of 2.7 smaller than the gas phase *B* value was required. One possible interpretation involves rotation not of free SF_6, but of a small “snowball” consisting of the SF_6 guest and a shell of 6−8 He atoms, embedded in a liquid helium cluster[98] (See Figure 9b). The rotationally resolved spectrum also served as the first direct temperature probe of the “doped” helium cluster, assuming temperature equilibration through evaporation of helium atoms from the cluster following SF_6 capture.[95] The experimental value of 0.37(5) K from a fit to the spectrum agrees remarkably well with the theoretical value of $T \approx 0.32$ K for pure helium clusters.[100] The Scoles’ group recently used the pick-up technique to introduce Na atoms as well as Na_2 dimers into large helium clusters, monitoring their presence using laser-induced fluorescence.[101,102] Particularly interesting are the spectra of sodium dimer, which have an appearance quite similar to what is usually observed in conventional matrix isolation spectroscopy. As illustrated in Figure 10, they exhibit what appears to be sharp zero-phonon lines and broad, unstructured phonon sidebands.

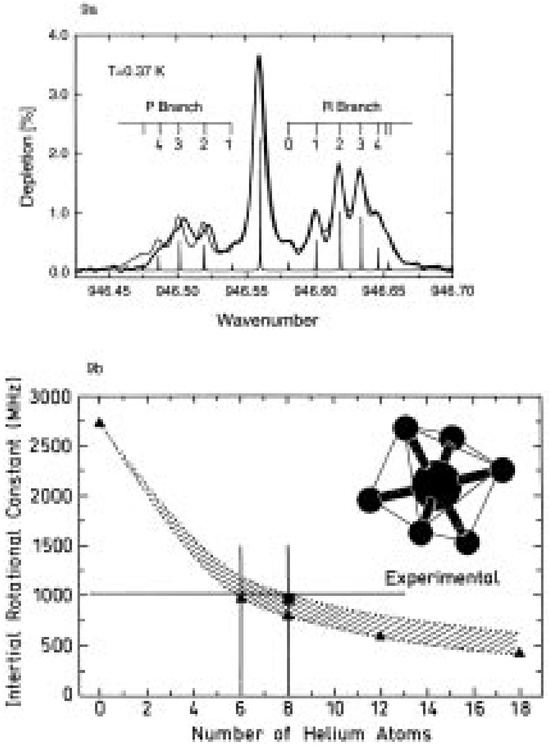


Figure 9. (a) The absorption spectrum of SF_6 embedded in He droplets (heavy solid line). The lighter solid line is a spherical top simulation with rotational constant $B = 0.0340$ cm^{-1}, Coriolis coupling constant $\zeta = 0.693$, centrifugal distortion constant $D = 3.75 \times 10^{-4}$ cm^{-1}, and $T = 0.37$ K. A stick spectrum is also shown to emphasize the rotational assignment. (b) A comparison of the calculated rotational constants for different numbers of rigidly attached helium atoms with the experimental result of 1019-(30) MHz. The solid triangles correspond to a S−He distance of 4.5 Å while the solid square was calculated based upon an estimate of the S−He distance from Pack et al. Overall the experimental rotational constant is consistent with 6−8 attached helium atoms. The inset shows an SF_6 molecule with its eight 3-fold sites. From M. Hartmann, R. E. Miller, J. P. Toennies, and A. Vilesov: *Phys. Rev. Lett.* **1995**, *75*, 1566, and *Science*, to appear in 1996.

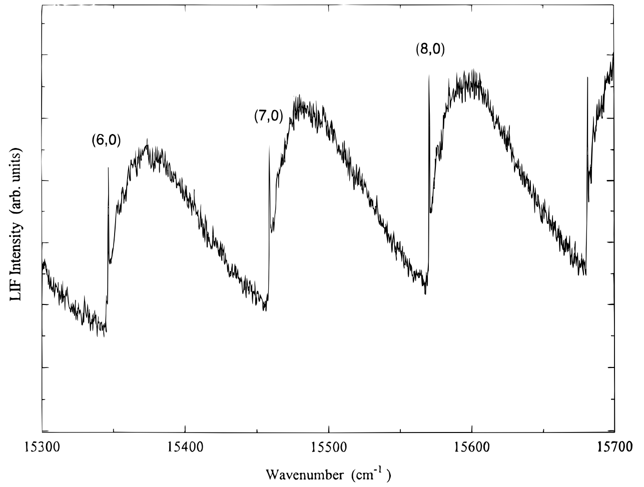


Figure 10. The laser-induced fluorescence spectrum recorded at 5 GHz resolution of the $A^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ transition of $Na_2\,He_N$. The (6,0), (7,0), and (8,0) vibronic bands of this transition are displayed. Each band consists of a sharp (≈1 cm^{-1} wide) line and an 80 cm^{-1} broad wing extending to the blue, very similiar in appearance to the zero-phonon lines and phonon side bands, respectively, observed in conventional matrix isolation spectroscopy. From F. Stienkemeier, J. Higgins, W. E. Ernst, and G. Scoles: *Phys. Rev. Lett.* **1995**, *74*, 3592.

Interesting in this context are studies of impurities in helium by Gordon and co-workers.[103] In their experiment the “impurities” to be studied: Ne, Ar, Kr, Xe, N_2, or N atoms produced in a liquid nitrogen cooled discharge are introduced from a gas phase jet into superfluid helium (He II) near 1.5 K. After completing the sample preparation, they observe that if the temperature is slowly increased, the liquid He evaporates, leaving behind a white solid. This solid is then stable until the temperature is further increased to 8−9 K, at which point an “explosive” decomposition of the solid sample takes place. Analysis reveals that the gases resulting from the decomposition consist predominantly (>90%) of helium. They interpret this observation in terms of an impurity-stabilized solid phase of helium, consisting effectively of “snowballs” of helium atoms “bound” to the central impurity. In this picture, the helium interact more strongly with the central atoms, but the entire “snowball” exhibits to the outside, a weakly interacting helium potential and can be to some extent viewed as a very heavy helium atom. This impurity-stabilized solid might also prove to be an interesting medium for spectroscopic studies. Gordon and co-workers have reported some preliminary results of luminescence believed to be due to nitrogen atom $^2D{-}^4S$ transition in the impurity stabilized solid, as well as laser-induced fluorescence of metastable Ne atoms.

Another weakly bound, “quantum” solid is molecular hydrogen. It is a fascinating material, and comparisons of properties of atoms and molecules in hydrogen matrices with those in more conventional solid rare gases or nitrogen are bound to provide interesting new insights. One interesting aspect is the existence of several isotopic species: even discounting the radioactive tritium, H_2, HD, and D_2 are solids with widely differing properties.[104,105] Another potentially interesting aspect is the existence of o-H_2 or p-D_2 in a metastable $J = 1$ rotational state. The isotopes of hydrogen are characterized by large differences in their vibrational frequencies. The molecules in the solid are known to be able to rotate relatively freely, and again there are large differences in their rotational constants. In this way one might expect a large effect of the isotopic nature of the host matrix on the nonradiative relaxation of the guest molecule.

A series of matrix studies in D_2 and H_2 solids was reported by Fajardo et al.[106] The major motivation of their studies was actually the question of energy storage and increase of the specific impulse of rocket fuels: in principle the amount of energy available per unit of mass. Most effective fuels are naturally highly reactive species with low atomic or molecular masses. They have therefore used laser vaporization to trap light metal atoms in rare gases, as well as in molecular hydrogen.[107] According to the authors, the laser vaporization technique was essential to isolate lithium atoms in the lighter host matrices: neon, hydrogen, or deuterium. They interpret this observation by suggesting that the high kinetic energy of the atoms in the laser generated plasma is necessary to penetrate the “accretion deposition layer” near the matrix surface, and thus avoid loss of the isolated guests due to their mobility and recombination processes. It appears more likely that the difficulties in depositing matrices containing atomic lithium are due to heating of the surface by thermal load from the hot lithium source. It would be interesting to try deposition of lithium atoms with our pulsed supersonic expansion laser vaporization source, where the atoms are thermalized and cooled prior to deposition, but where there are no hot furnace surfaces which might heat the matrix surface. Besides the spectroscopy of atomic species, studies of molecular guests in "quantum solids" should also be interesting. Recently the fluorescence of molecular O_2 in solid hydrogen and deuterium was investigated by Apkarian and co-workers.[108]

This and other pioneering spectroscopic studies of defects in quantum liquids and solids should stimulate fruitful theoretical studies in this area. It is clear from these results, as well as from work from several other labs, that the laser vaporization technique is extremely useful for the study of atomic and molecular species in these fascinating quantum hosts.

IV. Matrix Isolation Spectroscopy of Molecular Ions

Due to the high energies needed for their production and to their high reactivity, molecular ions are rather elusive species, and special techniques are needed for their studies. Compared with other methods for investigating molecular ions, matrix isolation has a number of advantages. It permits the ionic species to be accumulated and stored over long periods of time, and in this way the detection sensitivity can be enhanced. For optical detection, large spectral areas can be explored in a relatively short time, which makes initial search for unknown transitions much less tedious than in the gas phase.

The technique also has a number of drawbacks. In the first place the matrix guests are not really "isolated", but they interact with the host matrix, and for charged species this interaction is particularly strong. In general, relatively unperturbed spectra can be hoped for only if the ionization potential of the host exceeds the electron affinity of the guest by at least several electronvolts. An ideal matrix in this sense would be helium, which however cannot be solidified under ambient pressure (see section on "quantum hosts"). For most purposes the best available matrix material is therefore neon, which with its relatively high ionization energy (21.559 eV) is adequate for most organic and many inorganic species.[109−111]

A second difficulty with matrix isolation is that for previously unknown species the unambiguous identification of the carrier of a given spectrum may be quite difficult. The elemental composition can often be established using isotopic substitution, provided suitable isotopes are available. Some information about the charge state of the carrier can be obtained with the help of its photolytic behavior. In general, detaching electrons from negatively charged species requires little energy, and easy photolysis by near-infrared or visible radiation may suggest that the carrier is an anion. Cations with one bonding electron missing are usually less stable than the corresponding neutral compounds and are therefore easier to destroy by UV radiation. Tests of this nature should however be used with caution. There are also many labile neutral species which may fragment or isomerize even when exposed to infrared radiation. If the matrix contains cations, then also anions or trapped electrons maintaining the overall neutrality must be present. The electrons set free by infrared photodetachment may then react with the cations, destroying them also. Perhaps the most useful aid in assigning unknown bands or spectra lies in comparison with state of the art *ab initio* theoretical computations.

Matrix ion spectroscopy has also been previously reviewed on many occasions[112−114] and even here a comprehensive review is beyond the scope of this chapter. Our goal is to present only a selection of some new developments, and discuss some of the more recent work in this area.

A. Ion Sources for Matrix Isolation Spectroscopy

Prerequisite for successful ion studies is a suitable source of ionic species. The ionic concentration needed for successful spectroscopic characterization naturally depends on the optical properties of the ion to be studied and the sensitivity of the technique employed for its detection. For highly fluorescent ions with sharp electronic spectra, extremely low concentrations can be detected. The detectability extends certainly down to 1×10^{12}, and experiments aimed at single ion detection have at least been contemplated and have probably a fair chance of success.

Many of the earlier matrix experiments on ions or transients involved microwave discharges. In some of these experiments a dilute mixture of the matrix gas with a suitable parent compound to be fragmented or ionized was discharged. Alternatively, only a low-pressure rare gas, Ar, Kr, Xe, or a H_2/He mixture was discharged, and the high-energy vis−UV radiation from the discharge was used to photoionize the sample through an LiF window. In situ photolysis after completed sample deposition with such a low power discharge lamp for 5−30 s is typically entirely adequate to obtain excellent LIF emission and fluorescence excitation spectra. By using the "waveguide technique" with its long (≈20−30 mm) absorption path,[115,116] even visible or UV absorption spectra of ions with sharp electronic spectra can be readily obtained.

When a less sensitive technique, such as infrared spectroscopy, is to be used, or when the transition to be studied is weak or broadened, efficient methods of ion generation are needed. There is naturally a limit to concentrations of ions with their strong Coulombic interactions which can be stabilized in the weakly bound rare gas matrix. A number of methods have now been developed and optimized with which observation of ionic infrared spectra is feasible. One way to increase the ion production efficiency is to photolyze the sample continuously during the deposition. The Lyman α line of H atoms or the resonant Ar or Kr radiations were the wavelengths most often used, with the sample being photolyzed through an LiF or MgF_2 window. A distinct drawback of such a photolysis method is that the available photon energy

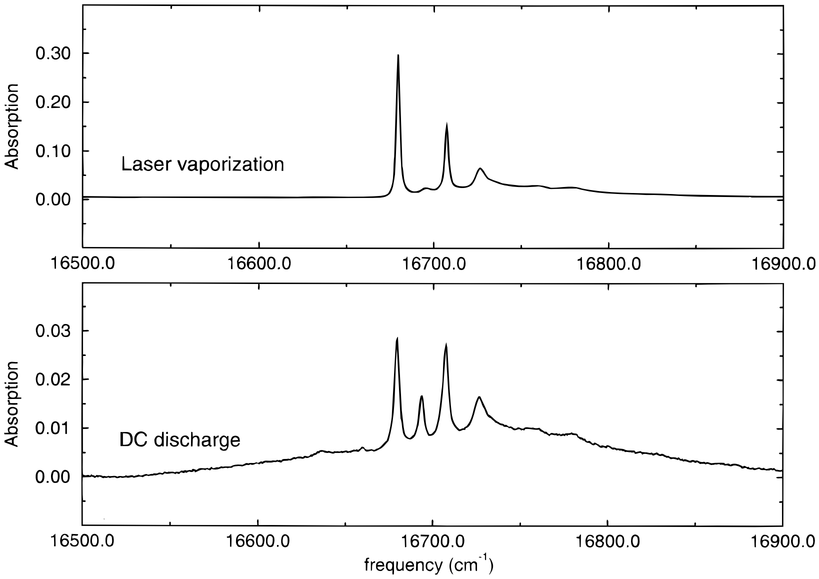


Figure 11. Part of our Fourier-transform visible spectrum comparing the origin region of the $A^2\Pi_g \leftarrow X^2\Pi_u$ transition of $C_4N_2^+$ in a neon matrix at 6 K produced in a laser-induced plasma (top) or pulsed DC discharge (bottom) from a gaseous sample of C_4N_2 in neon. Note that the ion generation is about 1 order of magnitude more efficient using laser vaporization. See text (section IV.A).

is limited by the transparency of the lamp window. Furthermore the window tends to develop color centers, and the transparency decreases rapidly with time.

In a long series of experiments, Jacox and co-workers[117] have used an arrangement where the pure matrix gas itself is discharged and the precursor species deposited separately. Using this arrangement they were able to study numerous small ions. Andrews and co-workers[118] have realized that by using an open end discharge tube both as a source of radiation and of the matrix gas they can avoid the transparency problem, and used this idea in a similar series of experiments.[118−120] With both arrangements, efficient fragmentation and ionization was observed. Some controversy actually developed as to how much of this effect is due to the intense radiation emanating from the discharge region and how much is caused by the Penning ionization and by interactions with the metastable rare gas atoms. The advantage of both techniques is that they are not limited by the window transparency, and therefore, also the much more energetic metastable Ne atoms (16.8 eV) and neon resonance radiation capable of ionizing most molecules can be used.

A similar arrangement with an open-tube neon resonance lamp was later very productively used by Knight and co-workers in a series of ESR studies of matrix isolated ions and radicals.[36,112,121,122] Besides the microwave sources, a corona discharge source of the type developed for gas phase studies by Engelking et al.[123,124] was also adapted for matrix work by Ault and co-workers.[125]

Much higher ion densities than in continuous discharges can be generated in a pulsed DC discharge, and several ion and transient sources of this type have been developed. One such source, employed in our laboratory both for gas-phase and matrix studies combines a self-igniting pulsed discharge with a supersonic expansion.[32] A pulse of matrix gas mixed with a suitable parent compound streams through a discharge channel and triggers a discharge between two high-voltage electrodes. The species produced in the discharge are cooled by the adiabatic expansion into vacuum and can be either probed in the gas phase by laser-induced fluorescence or accumulated in the matrix for subsequent spectroscopic studies. As mentioned in a previous section, a further significant advantage of this arrangement is that the pulsed deposition yields matrix samples of excellent optical quality. We have employed this technique in a series of studies of ions and molecules of astrophysical interest—particularly long linear chain carbon-rich species.[31] A similar pulsed glow discharge, but working at lower backing pressures and without the supersonic expansion, was described by Szczepanski et al.[126]

A further method which is steadily gaining in popularity for studies of ions is laser vaporization, which we discussed in the section dedicated to this method. In fact we have reported the first study of ions using this technique almost a decade ago, in 1987 when we generated the C_2^-, and C_2^+ ions (as well as neutral C_2) in a neon matrix by laser vaporization of graphite.[75] Today, it probably represents the most versatile method of ion production. (See Table 1.) An interesting variant of laser vaporization specifically for studies of molecular ions was recently developed in our laboratory. If the vaporizing laser impinges on a metal electrode, and a molecular precursor is added to the carrier gas streaming through the flow channel, very efficient ionization of this precursor takes place. This was found to occur for all metals tried, in spite of the fact that the ionization potential of the precursor molecules was higher than that of the metal. We speculated that in the vaporization region metastable rare gas atoms are formed by charge transfer with multiply ionized metal atoms, and these then Penning ionize the parent. In any event, the method turned out to be the most efficient mode of production for a number of organic molecular ions, as exemplified in Figure 11, which shows the origin region of the optical absorption spectrum of $C_4N_2^+$.

B. Spectroscopic Methods

1. Electron Spin Resonance

Electron spin resonance (ESR) is one of the spectroscopic techniques used extensively in combination with matrix isolation, and several excellent review articles focus specifically on the application of this method.[36,127] Its great advantage is that it is sensitive selectively to open-shell species and thus permits detection of radicals, ions, and similar species with unpaired electrons without any interference of even a large excess of closed-shell species which might be present in the matrix. This great advantage is naturally a drawback at the same time—it is of no use for closed-shell molecules. Even its applicability to open shell molecules is not quite universal, but fails for species with degenerate ground states and unquenched orbital angular momentum. In such cases, for instance in linear molecules in Π or Δ states, the anisotropy of the **g** tensor leads to extreme broadening of the transitions. Even the failure to detect the X $^2\Sigma_g^+$ ground state of the C_2^- anion by ESR, even though it is one of the easiest anions to produce and detect by electronic fluorescence or even absorption spectroscopy, was attributed to the proximity of, and mixing with, a low-lying A $^2\Pi_u$ electronic state.

As noted above, the technique provides information about the ground electronic state, and if suitable isotopic studies can be carried out and both the **g** and **A** tensors can be obtained, they provide a good characterization of the density distribution of the unpaired electron, and of the electronic wave function. One difficulty is that gas-phase data for most of the small radicals studied in the matrix is not available, and the calibration of matrix effects is thus lacking, but the matrix results can be tested against **A** tensors derived from ab initio wave functions. ESR can thus provide valuable information about the molecular symmetry and structure, but does not provide much of the data which chemists and physicists would like to have: information about vibrational constants or bond lengths.

Laser vaporization permits easy generation of species which would be difficult to produce by other methods, and this was also reflected in recent matrix ESR studies. Several years ago, we showed that ionic clusters of semiconductor materials, such as gallium or indium phosphide, germanium or silicon, are efficiently generated using this technique.[128] Recently in particular the group of Knight has reported the ESR spectra of many such species: e.g., Si_2^+,[129] Ge_2^+,[129] $GaAs^+$,[130] and GaP^+.[131] (See Table 1.)

Among other interesting recent ESR work on molecular ions, one might mention the study of the NH_3^+ [132] and methanol, CH_3OH^+ [122] molecular cations produced by X-ray irradiation, and the investigations of various metal dimer[133−136] and metal oxide cations[136] by Weltner and co-workers. (See Table 1.) A series of interesting studies dealing with ESR spectra of various organic anions produced by photoinduced electron transfer between the precursor molecule and simultaneously deposited Na atoms was reported by Kasai et al.[137−143]

2. Infrared and Optical Absorption

As mentioned above, the problem with optical absorption spectroscopy in general, and infrared spectroscopy in particular, is the lower relative sensitivity of the technique, and also the difficulties associated with identification of the elemental composition and charge state of the observed species. In spite of these experimental difficulties, a number of interesting optical absorption studies of molecular ions have been reported in the last few years. Jacox and co-workers have reported a series of thorough investigations, in which they succeeded in observing the vibrational spectra of a number of small inorganic cations and anions. Among the species studied are, for instance the anion and cation of carbon dioxide, CO_2^+ and CO_2^-,[144] as well as CO^+, and the ionic forms of the carbon monoxide dimer, $C_2O_2^+$ and $C_2O_2^-$.[145] They also reported the infrared spectra of the HCN^+ cation and its HNC^+ isomer and observed also the IR absorption of the CN^- anion.[146]

Another interesting study involved the ionized nitric oxide and its dimers, NO^+, NO^-, $ONNO^+$, and $ONNO^-$,[147] species of some interest from the point of view of atmospheric chemistry. Interestingly, the frequencies assigned to the anion dimer are in almost perfect agreement with those determined for the cation by high-resolution gas-phase photoelectron (ZEKE) spectroscopy.[148] Unless this is a very unusual coincidence, the matrix spectrum would have to actually be that of cation, demonstrating again the difficulty of determining the charge state of matrix isolated species. This finding necessarily throws the tentative assignment of a neon matrix infrared absorption at 1787.3 cm^{-1} to $ONNO^+$ further in doubt. A thorough theoretical study of the NO_2^x systems would certainly be very desirable to unambiguously settle this question.

Another area of considerable current interest involves matrix studies aimed at the spectroscopy of polycyclic aromatic hydrocarbons (PAHs). The main motivation of these studies is the elucidation of the diffuse interstellar bands (DIBs). Light arriving to us from distant luminous objects exhibits numerous absorptions due to interstellar matter. The first of the DIBs was noticed in 1921 and presently more than 120 DIBs in the 430−860 nm region,[149,150] in addition to a few bands in the near-infrared,[151] are known. One of the numerous possible assignments proposed for at least some of these bands involves the PAHs—compounds with fused aromatic rings such as naphthalene or anthracene—and ions or radicals derived by their ionization or partial dehydrogenation. At least three research groups are currently very active in this area and have attempted to measure the infrared as well as visible spectra of these species: Allamandola at AMES, Léger and d'Hendecourt at Orsay, and Vala and co-workers.

Allamandola and co-workers have done a lot of research on small and very small PAH cations in neon and have reported absorption spectra from the infrared to the UV.[152−156] From their data they conclude that the cations under investigation are largely unperturbed by the environment and that the relative absorption band intensities are in much better agreement with the observed DIBs than those of the corresponding neutral species. On the other hand, Léger and d'Hendecourt observed that the relative IR band intensities of the neutrals clearly depend on the physical environment—solid, matrix or gas phase[157]—whereas the different line positions can be explained as temperature effects.[158] Furthermore they show that there is a good similarity between astronomically observed unidentified infrared bands and those of larger neutral PAHs if they are partly dehydrogenated. Like Allamandola et al., Vala and co-workers concentrate on matrix-isolated naphthalene, anthracene, and pentacene cations and also observed that the relative intensities of the IR bands are quite different from those of the neutral analogues.[159−161] They came to the not too surprising conclusion that neither the pentacene neutral nor its cation are the carriers of any of the DIBs.

Several arguments have been given, suggesting that PAHs are unlikely to be the dominant species in the interstellar gas and that, on the other hand, cumulenic carbon chains are promising candidates for the carriers of the DIBs.[162,163] Maier and co-workers have also recently proposed the family of highly unsaturated hydrocarbon chain molecules as potential carriers of the DIBs.[164,165] They deposited mass-selected species of type $C_nH_m^-$ where $n = 2-16$ and $m < 3$ with concomitant Hg lamp irradiation and recorded absorption spectra in the near-infrared, visible, and ultraviolet regions. For the hydrocarbon chains with 6 to 16 carbon atoms, the number of coincidences in the 600−860 nm region is striking: 17 bands overlap with the DIBS to within ± 36 cm^{-1}. Also consistent with astronomical observations is the lack of absorption bands in the ultraviolet. Through their most recent absorption studies of mass-selected species in neon matrices, they can now attribute these bands to specific linear carbon chains , e.g. the DIBs at 722.40, 802.62, and 864.90 nm can be assigned to the origin bands of the electronic transitions of $C_{10}H$, $C_{12}H$, and $C_{14}H$.[166] Also relevant in connection with the DIBs is their observation that the $C_{2n}H$ ($n = 2-7$) chains are stable to UV photons down to 200 nm.

3. Laser-Induced Fluorescence

Absorption spectra of matrix-isolated samples are often complicated by site effects and inhomogeneous broadening, and in addition they suffer from relatively low sensitivity, even if the waveguide technique can be used. All of these problem can be eliminated for species with high fluorescence quantum efficiency with the help of the laser-induced fluorescence technique. As noted above, its ability to detect matrix-isolated species extends in favorable cases to single molecules, and the problems with sites and inhomogeneous broadening can be eliminated, and in fact often used to obtain additional information.

An extremely useful and powerful feature of our FT-IR setup, made use of extensively in our ionic studies, is the ability to automatically record three-dimensional (3D) spectra of the type shown in Figure 12 for the $C_8H_2^+$ cation. The necessary data is obtained by scanning, under computer control, the excitation laser stepwise, and automatically recording an FT emission spectrum at each step. A computer program written for this purpose then processes the data to generate the constant intensity contour plot shown in the figure. Such plots are extremely informative and contain all the spectroscopic information not only about both the excited and the ground states of the emitting species, but also about their isotopic content, relaxation processes, and in particular about the inhomogeneous site distribution. Particularly valuable is the ability to distinguish inhomogeneous matrix site effects from intrinsic spectroscopic properties of the isolated molecules.

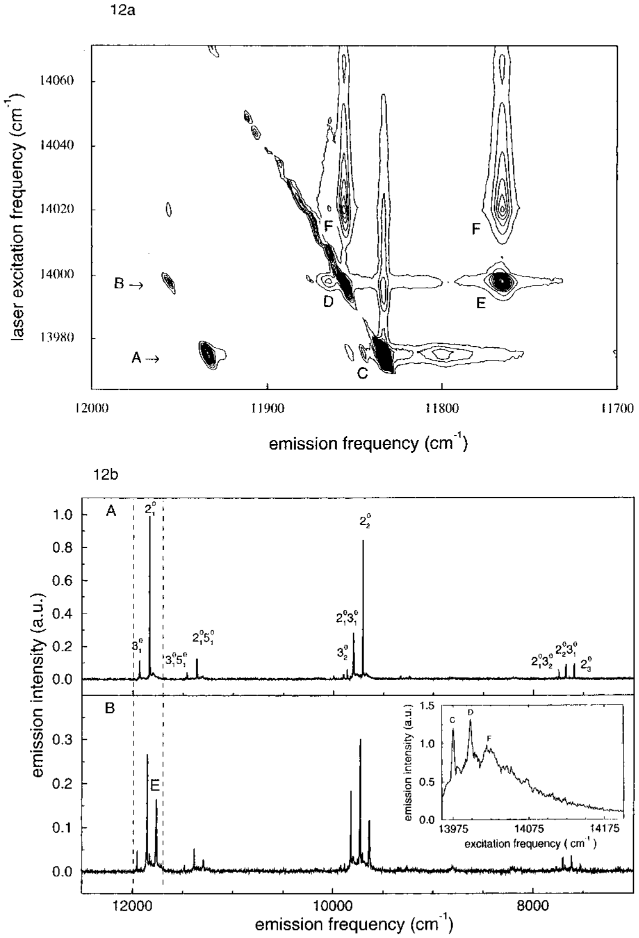


Figure 12. (a) Part of the three-dimensional laser-induced fluorescence spectrum of the $A^2\Pi_u \leftarrow X^2\Pi_g$ transition of $C_8H_2^+$ in solid neon. The interpretation of these plots is described thoroughly in section IV.B.3. Briefly the tunable laser is stepped (y) and the Fourier-transform emission (x) recorded at each step, the emission intensity (z) being shown as contours of equal intensity. Part b shows a larger region of the near-infrared emission for site-selective excitation of site A and B respectively. The area shown between dashed lines is equivalent to the horizontal cuts A and B through the three-dimensional surface in a. The insert in b shows the laser excitation spectrum in the origin region, equivalent to the sum of all vertical cuts through the three-dimensional surface. For vibrational assignments, see ref 31.

In such a plot the ordinate gives the wavelength of the exciting laser and the abscissa the emission wavelength, with the contours connecting points of equal fluorescence intensity. A horizontal cut through the three-dimensional surface represents an emission spectrum observed with the laser tuned to the frequency given by the ordinate (Figure 12b). Vibrational (and rotational) relaxation processes are, particularly for larger molecules, usually much faster than the radiative rate, and predominantly vibrationally relaxed emission from molecules thermalized to the temperature of the matrix (5−7 K in our experiments) is observed. Whenever the laser is tuned to an absorption band of a given molecule (in a given matrix "site"), an identical emission spectrum is therefore observed. A vertical cut through the plot thus gives the absorption (or better laser excitation or yield) spectrum of the molecule in the given site. Figure 12a thus shows changes in a section of the emission spectrum between the broken lines in Figure 12b, that is 400 cm^{-1} of the total range of > 6000 cm^{-1} studied, with the laser being scanned about 100 cm^{-1} (see inset of Figure 12b) of a total range of about 5000 cm^{-1} examined, that is less than 0.5% of the complete data set.

When the molecule is present in two or more different "sites", moving the laser from absorption due to one site to the spectrally shifted site will result in selective emission of that site, shifted by the same margin. Each of the little "islands" in the 3D plot represents a vibronic transition of a given species. Islands due to different sites will be shifted diagonally in the plot (45° if the abscissa and ordinate scales are the same). If the inhomogeneous broadening of the lines of a given "site" is comparable to the resolution of the experiment, the "islands" will be more or less circular. Oblong, diagonally oriented islands indicate that the inhomogeneous broadening of the transition is larger than the resolution.

Specifically for $C_8H_2^+$, one finds that the two sharper maxima, C and D, shown in the insert in Figure 12b correspond to two different matrix sites as shown by two diagonally displaced islands (C and D in Figure 12a). Furthermore, one can see a different spectroscopic behavior of the two sites, with one of the sites having subsidiary emission bands shifted by about 80 cm^{-1} to lower energy (see the island marked with E in Figure 12a and the peak marked E in Figure 12b) and also subsidiary broader absorption bands shifted by 30 cm^{-1} to the blue (see the broader "islands" marked in Figure 12a with F and the broader peak in the Figure 12b insert marked with F). Quite remarkably, the same observation, that is two major sites, with only one of them showing this behavior with spectrally shifted side bands was observed for a whole series of similar, linear chain carbon species in neon: $C_{2n}H_2^+$,[31,167] $C_{2n}N_2^+$,[168,169] and $HC_{2n}CN^+$ cations.[170] We have proposed that this similarity in site distribution and behavior can only be caused by some characteristic property of the matrix itself, and suggested that the two sites correspond to the guests isolated in FCC and HCP regions of the solid neon matrix, respectively. The subsidiary levels, shifted by some 80 cm^{-1} in the ground state, and by about 20 cm^{-1} in the excited states, are due to the $\Omega = {}^1/_2$ and ${}^3/_2$ components of the two $^2\Pi$ states, with the ${}^1/_2 - {}^3/_2$ or $\Delta\Omega = \pm 1$ transitions becoming more strongly allowed due to the change in the site symmetry.

V. Deposition of Mass-Selected Species

One of the problems in exploring complex polyatomic ions or radicals, such as the PAHs, or polyacetylene-derived species discussed above, or for instance metal or semiconductor clusters, is that they are rarely produced selectively. In most cases one obtains complex mixtures of species with various number of atoms, elemental composition or charge. The assignment of the observed spectra then becomes extremely tedious at best, and almost impossible in many cases. One obvious way to solve this problem would seem to be to deposit the desired species as a mass-selected ion or molecular beam. With the information about the mass and possibly the state of charge of the species, the assignment should become much easier. The idea of mass-selective deposition is almost as old as the matrix technique itself, but its implementation faces tremendous experimental difficulties.

There are at least three major problems. In the first place, in order to be able to detect the isolated species, one needs either an extremely sensitive detection technique, or a very intense ion beam. The generation of sufficiently intense mass-selected beams was one serious obstacle. The second problem involves decelerating the beam and "soft landing" the species of interest in the matrix. To accomplish effective mass selection, one typically has to accelerate the ions to appreciable energies exceeding hundreds of electronvolts. On the other hand, the binding energy of two rare gas atoms is of the order of 10 meV. Unless the ions impinging on the matrix are sufficiently slowed down, they can fragment on impact at the surface. Even if for strongly bound ions fragmentation can be avoided, the ion kinetic energy can result in surface melting and vaporization of a number of matrix atoms. The guest ion can then penetrate deep into the matrix and recombine or react with some of the other guests or impurity molecules already present, and the selectivity can thus be lost. A third elusive problem is maintaining the overall neutrality of the matrix, opposing the goal of accumulating a high number density of a specific ion. In spite of these formidable experimental problems, in the last few years considerable progress has occurred in this field, and several groups have succeeded in depositing and detecting mass-selected species in the matrix.

A triple quadrupole apparatus, initially intended for gas-phase studies of size-selected clusters, was developed at the Ecole Polytechnique Federale in Lausanne by Fayet and Wöste.[171,172] Rivoal et al. interfaced this source to a cryostat and modified the apparatus for matrix isolation.[173] The setup was then used in a series of studies of matrix-isolated size-selected metal clusters and continuously improved. In the early experiments, currents of the order 0.1 nA of the Ag_3^+ and Ni_3^+ trimers were deposited, but this proved insufficient for optical detection of the clusters.[173] Also in an experiment by Lindsay et al. using a similar setup, only atoms were detectable.[174] In subsequent improved experiments,[175,176] the geometry of the high-energy sputter source with 10 mA primary beam of 20 keV Kr^+ ions was changed. The ions produced in these studies, Au_n or Ag_n ($n \le 3$), were extracted at 90° to the primary beam and injected into a single quadrupole filter for mass selection. Ions exiting the quadrupole were confined and directed toward the sapphire matrix substrate by an electrostatic lens, and after deceleration using a grid in front of the window, codeposited with krypton matrix gas. Currents decreased from over 50 nA for the monomers Au^+ and Ag^+ to about 1 nA for the tetramers. To neutralize the ions, electrons emitted by a tungsten filament were used. The deposited species are probed by fluorescence and yield spectroscopy. In the early experiments, considerable fragmentation apparently took place, in spite of the attempts to “soft land” the ions. Further refinements permitted depositing observable amounts of size-selected silver clusters up to $n = 21$ with beam currents ranging typically from 2 to 4 nA. The UV spectra of these species recorded from 2.1−6.2 eV exhibited 1−3 absorption bands between 3−4.5 eV. These were interpreted as collective plasmon excitation using a model considering only s electrons. The appearance of more than one band was attributed to the ellipsoidal shape of the clusters.[176]

Another apparatus for mass-selected experiments was built by Lindsay, one of the participants of the original Lausanne collaboration, and co-workers at the City College in New York. In this new setup, the quadrupole mass spectrometer was replaced by a Wien velocity filter, in which an electrostatic deflection force on the ions is compensated by the velocity dependent Lorenz force of a perpendicular magnetic field. The velocity filter, while having a relatively low mass resolution, seems to permit higher ion currents than the quadrupole mass spectrometer. Using this new apparatus, Lindsay, Lombardi, and co-workers were able to perform a series of interesting studies of absorption and resonance Raman spectra of a number of small metal clusters, including V_2,[178] Hf_2,[179] W_2,[180] Co_2,[181] Zr_3,[182] Ta_2,[183] and Ta_4.[184]

Another apparatus for mass-selected studies was developed by Leroi and Allison. They employed commercial anion and cation sources and also used a modified quadrupole residual mass analyzer to obtain the mass-selected ion beam.[185] In preliminary studies they tried to deposit a mass-selected CS_2^+ beam. After deposition at >1 nA for >5 h they were able to obtain the LIF excitation spectrum of the CS_2^+ cation. Even after 48 h of deposition, however, only the absorption bands of the neutral parent CS_2 and of the diatomic CS could be observed in the infrared. The authors interpret this observation in terms of neutralization of the CS_2^+ ions, which results in neutrals energetic enough to fragment to CS+S.[186] The same group recently reported the successful infrared detection of CF_3^+ after a 10−25 h codeposition of a 15−25 nA ion current with argon and neon.[187,188]

Perhaps most successful in the area of matrix deposition and spectroscopy of mass-selected species was the group of Maier and co-workers. In their earliest experiments mainly absorption spectra of several small species which were already known from previous studies could be detected.[189,190] More recently however, Maier and co-workers have modified substantially their initial experimental setup and applied it to studies of species of astrophysical interest, and in particular the linear carbon chain molecules and their substituted derivatives.[166,191−194] The carbon chain species are generated in a hot cathode discharge source using a mixture of about 30% of the precursor molecules: diacetylene, cyanoacetylene, or dicyanoacetylene in helium. The ions generated in the discharge are accelerated, the beam is focused with the help of electrostatic lenses, deflected at 90°, and mass-selected in a quadrupole filter. Additional electrostatic lenses guide the selected species to the matrix surface. The authors find that a current of about >10 nA is needed for a successful optical characterization. They also conclude that the residual energy of the ions has to be maintained below about 50 eV, a value which still does not seriously degrade the beam current, but avoids an excessive fragmentation. For some ions, less abundant in their discharge source, they find they have to degrade the mass resolution to 5 m_u (AMU, atomic mass units) to attain adequate beam currents. This permits selection of clusters differing in the number of carbon atoms, but some uncertainty remains as to the degree of hydrogenation. Typically the authors operate with ion currents near 25 nA, from which they estimate final ion concentrations in the neon matrix of up to 10^{15} cm^{-3}. To characterize the deposited species they use the waveguide absorption technique[115,195] in the visible and UV range, and an FT-IR spectrometer in the near-infrared and infrared below 10 000 cm^{-1}.

With this setup, they were able to measure for the first time the optical absorption spectra of numerous long linear carbon chain species; HC_kH^+, (k = 4−16),[191,194] the neutral $HC_{2n+1}H$ (n = 2−7) species,[194] $H-(C{\equiv}C)_n-CN^+$ (n = 2−6) and $NC-(C{\equiv}C)_n-CN^+$ (n = 1−5).[192] This work is complementary to our recent laser-induced fluorescence studies of $H-(C{\equiv}C)_n-CN^+$ (n = 2−3)[170] and $NC-(C{\equiv}C)_n-CN^+$ (n = 1−3)[168,169] and $H-(C{\equiv}C)_n-H^+$ (n = 3−5)[31,167] in solid neon.

They have also recently reported spectra of the mass-selected, matrix-isolated anions C_{2n}^- up to n = 10, as well as of the corresponding neutral C_{2n} molecules up to n = 7, and of the $C_{2n}H$ radicals up to n = 8.[166,192] (See Table 4.) For anion production a different hot-cathode discharge source was used[196] and the precursor gas diluted with argon. The ion current needed (≈10 nA) required degradation of the mass resolution to about 3 m_u (AMU). Thus pure carbon ions could not be separated from their hydrated forms. Hence in complementary experiments, they eliminated the hydrogen-containing species by employing instead a cesium negative ion sputter source[197,198] to sputter graphite. They also compared these absorption spectra with those produced from the laser vaporization of graphite (without mass selection), alternatively exposed during deposition to an open microwave discharge of neon.

Beginning with the pioneering studies of Broida et al.[199] and Weltner et al.,[200] several attempts have been made in assigning the visible transitions of the important carbon cluster molecules.[63,201] Using typically either electrical heating or laser vaporization of graphite, followed by subsequent annealing cycles, numerous assignments were proposed on the basis of intensity correlations with the known infrared bands. The drawbacks of this method are clear, and even though the first band of C_3 was seen in the emission spectra of comets as early as 1881, until quite recently, C_2 and C_3 were the only carbon cluster species with definitively assigned electronic transitions.[31] One barrier here is the absence of observable fluorescence for the larger carbon clusters. Weltner observed already in 1966 “carbon cluster” absorptions

Table 4. Electronic Transition Energies of Various Ionic and Neutral Carbon and Hydrocarbon Chain Molecules in Neon Matrices (All Values in cm^{-1})

$^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$		$^2\Pi \leftarrow X^2\Pi$					
C_{2n}[a]	energy	C_{2n}^- [a]	energy	$C_{2n}H$[a]	energy	$C_{2n}H_2^+$	energy
C_4[b]	26323	C_4^-	21896	C_4H[c]		$C_4H_2^+$ [d]	19708
C_6[e]	19558	C_6^-	16458	C_6H	18854	$C_6H_2^+$ [f]	16570
C_8	15630	C_8^-	12933	C_8H	15848	$C_8H_2^+$ [f]	13975
C_{10}	13596	C_{10}^-	10338	$C_{10}H$	13852	$C_{10}H_2^+$ [g]	12080
C_{12}	11625	C_{12}^-	8006	$C_{12}H$	12492	$C_{12}H_2^+$ [h]	10703
C_{14}	10195	C_{14}^-	6849	$C_{14}H$	11554	$C_{14}H_2^+$ [h]	9548
		C_{16}^-	5784	$C_{16}H$	10821	$C_{16}H_2^+$ [h]	8620
		C_{18}^-	4833				
		C_{20}^-	4099				

[a] P. Freivogel, J. Fulara, M. Jakobi, D. Forney and J. P. Maier: *J. Chem. Phys.* **1995**, *103*, 54. [b] P. Freivogel, M. Grutter, D. Forney and J. P. Maier: To be published. [c] Ground state is $^2\Sigma$ instead of $^2\Pi$. $^2\Pi \leftarrow X^2\Sigma$ transition at 33800 cm^{-1}. See K. I. Dismuke, W. R. M. Graham and W. Weltner, Jr.: *J. Mol. Spectrosc.* **1975**, *57*, 127. [d] V. E. Bondybey and J. H. English: *J. Chem. Phys.* **1979**, *71*, 777. [e] Transition previously assigned to C_4. See W. R. M. Graham, K. Dismuke and W. Weltner: *Astrophys. J.* **1976**, *204*, 301. [f] A. M. Smith, J. Agreiter, M. Härtle, C. Engel and V. E. Bondybey: *Chem. Phys.* **1994**, *189*, 315. [g] A. M. Smith, J. Agreiter, and V. E. Bondybey: To be published. [h] P. Freivogel, J. Fulara, D. Lessen, D. Forney, and J. P. Maier: *Chem. Phys.* **1994**, *189*, 335.

at 19561.0 and 21651.6 cm^{-1} in neon,[200] which were assigned to C_4 by Graham et al.,[202] and later reassigned to C_2^-.[126]

We have observed the same absorptions in neon matrices containing carbon clusters produced both in electric discharge through diacetylene[31] and by laser vaporization of graphite. Unfortunately, no fluorescence could be detected upon resonant laser excitation of these absorptions. The recent absorption studies of Maier et al. on mass-selected carbon clusters in neon (so far on the even carbon species) provided an elegant solution to this problem, and could conclusively assign these absorptions to linear C_6. (See Table 4.)

Interesting is also the comparison of their mass-selected neon spectra with spectra produced by annealing of C_n containing matrices, or the spectra from laser vaporization. On the basis of the observed differences in the spectra, Maier et al. conclude that the ion-beam-deposited anionic and cationic carbon clusters form preferably the linear neutral species up to C_{14}, whereas the laser vaporization and annealing studies lead to the theoretically predicted more stable cyclic forms for the larger clusters.[166]

While at this time only a few from the numerous groups doing matrix isolation have actually implemented mass selection, these results show clearly that the experimental problems mentioned at the beginning of this section can be overcome. There is little doubt that mass selection will become an extremely useful technique in future matrix isolation studies.

VI. Summary

In this manuscript we have reviewed some of the more recent matrix isolation studies. Rather than attempting a comprehensive review, we have concentrated on several areas where we either believe the most significant advances were made or which lie in the direct sphere of interest of our own group. The recent developments show that matrix isolation will remain a useful technique for preliminary characterization of radicals, clusters, ions, and other reactive intermediates. In this respect, laser vaporization has provided a very powerful and versatile tool for generation of these species. The recent studies also show that the problems of deposition of mass-selected ions and species can be surmounted, and this will go a long way toward making identification and assignment of matrix spectra easier, reducing thus possibilities of errors and misassignments. Besides studies of transient species, the recent developments also indicate the shift of emphasis from pure spectroscopy toward trying to understand the details of the guest solvation and of guest−host interactions. Very interesting in this context should be studies in novel and unusual matrices, such as the so-called “quantum hosts”, for instance solid isotopes of hydrogen, and in solid or liquid helium. The survey of the literature shows that in spite of the fact that more than 70 years have elapsed since the early experiments of Vegard, and 40 since Pimentel has coined its name, matrix isolation remains a very viable and useful technique.

References

(1) Vegard, L. The auroral spectrum and the upper atmosphere. *Nature* **1924**, *114*, 357.

(2) Whittle, E.; Dows, D. A.; Pimentel, G. C. Matrix isolation method for the experimental study of unstable species. *J. Chem. Phys.* **1954**, *22*, 1943.

(3) Bondybey,V. E. ; Nitzan, A. Radiationless transitions in small molecules, Interstate cascading in matrix-isolated CN. *Phys. Rev. Lett.* **1977**, *38*(16), 889.

(4) Bondybey, V. E.; Brus, L. E. Nonradiative processes in small molecules in low-temperature solids. In *Advances in Chemical Physics*; Prigogine, R., Rice, S. A., Eds.; John Wiley & Sons: New York, 1980; Vol. 41.

(5) Breckenridge, W. H.; Jouvet, C.; Soep, B. Metal-atom/rare-gas van der waals complexes. In *Advances in Metal and Semiconductor Clusters*; Duncan, M., Ed.; JIA Press: Greenwich, 1995; Vol. 3.

(6) Stace, A. J. A monte carlo model for simulating the behaviour of a quantum harmonic oscillator embedded in a classical cluster, liquid or solid. *Chem. Phys. Lett.* **1995**, *232*, 283.

(7) Crépin, C.; Tramer, A. Rare-gas matrix as an infinite rare-gas cluster: a spectroscopic study of 9,10-dichloroanthracene in argon matrices. *Chem. Phys. Lett.* **1990**, *170*(5,6), 446.

(8) Wurfel, B. E.; Thoma, A.; Schallmoser, G.; Lammers, A.; Bondybey, V. E. Absorption and fluorescence of Tl atoms in rare gas matrices. *J. Chem. Phys.* **1994**, *100*(11), 8003.

(9) Andrews, L., Moskovits, M., Eds. *Chemistry and Physics of Matrix-isolated Species*; North Holland: Amsterdam, 1989.

(10) Clark, R. J. H., Hester, R. E., Eds. *Spectroscopy of Matrix Isolated Species*; John Wiley & Sons: Chichester, NY, 1989.

(11) Dhez, P.; Jaegle, P.; Leach, S.; Velghe, M. Some characteristics of the extreme ultraviolet spectrum emitted by the plasma produced by laser impact on an aluminium target. *J. Appl. Phys.* **1969**, *40*(6), 2545 and references therein.

(12) Dietz, T. G.; Duncan, M. A.; Powers, D. E.; Smalley, R. J. Laser production of supersonic metal cluster beams. *J. Chem. Phys.* **1981**, *74*, 6511.

(13) Bondybey, V. E.; English, J. H. Laser induced fluorescence of metal clusters produced by laser vaporization: Gas phase spectrum of Pb$_2$. *J. Chem. Phys.* **1981**, *74*, 6978.

(14) Bondybey, V. E.; Miller, T. A. Vibronic spectroscopy and photophysics of molecular ions in low temperature matrices. In Miller, T. A., Bondybey, V. E., Eds.; *Molecular Ions: Spectroscopy, Structure and Chemistry*; North Holland: Amsterdam, 1983.

(15) Schaeffer, R.; Pearson, R. K. Reaction of carbon vapor produced by laser evaporation of graphite. *J. Am. Chem. Soc.* **1969**, *91*(8), 2153.

(16) Koerner von Gustorf, E. A.; Jaenicke, O.; Wolfbeis, O; Eady, C. R. The laser-evaporation of metals and its application to organometallic synthesis. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*(5), 278.

(17) Heaven, M. C.; Miller, T. A.; Bondybey, V. E. Laser spectroscopy of Pb$_2$ produced by laser vaporization. *J. Phys. Chem.* **1983**, *87*, 2072.

(18) Bondybey, V. E.; English, J. H. Laser excitation spectra and lifetimes of Pb$_2$ and Sn$_2$ produced by YAG laser vaporization. *J. Chem. Phys.* **1982**, *76*, 2165.

(19) Bondybey, V. E.; Heaven, M.; Miller, T. A. Laser vaporization of tin: Spectra and ground state molecular parameters of Sn$_2$. *J. Chem. Phys.* **1983**, *78*, 3593.

(20) Bondybey, V. E. Laser vaporization of silicon carbide: Lifetime and spectroscopy of SiC$_2$. *J. Phys. Chem.* **1982**, *86*, 3396.

(21) Heaven, M.; Miller, T. A.; English, J. H.; Bondybey, V. E. Laser induced fluorescence spectra of YAG laser vaporized Se$_2$. *Chem. Phys. Lett.* 91, 251, 1982.

(22) Bondybey, V. E.; English, J. H. Electronic structure and spectra of SnBi. *J. Chem. Phys.* **1983**, *79*, 4746.

(23) Bondybey, V. E.; English, J. H. Electronic structure and vibrational frequency of Cr$_2$. *Chem. Phys. Lett.* **1983**, *94*, 443.

(24) Gole, J. L.; English, J. H.; Bondybey, V. E. Laser spectroscopy of cooled metal clusters: Copper dimer. *J. Phys. Chem.* **1982**, *86*, 2560.

(25) Bondybey, V. E.; English, J. H. Laser vaporization of beryllium: Gas phase spectrum and molecular potential of Be$_2$. *J. Chem. Phys.* **1984**, *80*, 568.

(26) Bondybey, V. E. Laser-induced fluorescence and bonding of metal dimers. *Science* **1985**, *227*, 125.

(27) Bondybey, V. E.; English, J. H. Laser-induced fluorescence of the calcium dimer in supersonic jet: The red spectrum of Ca$_2$. *Chem. Phys. Lett.* **1984**, *111*, 195.

(28) Knight, L. B., Jr.; Generation and study of inorganic cations in rare gas matrices by electron spin resonance. In *Radical Ionic Systems*: Kluwer Academic Publishers: Boston, 1991; p 73.

(29) Lorenz, M.; Agreiter, J.; Smith, A. M.; Bondybey, V. E. Electronic structure of diatomic boron nitride. *J. Chem. Phys.* **1996**, *104*(8), 3143.

(30) Smith, A. M.; Lorenz, M.; Agreiter, J.; Bondybey, V. E. Electronic structure of diatomic boron carbide. *Mol. Phys.* **1996**, *88*(1), 247.

(31) Smith, A. M.; Agreiter, J.; Härtle, M.; Engel, C.; Bondybey, V. E. Rare gas matrix studies of absorption and fluorescence of reactive intermediates in discharges through acetylene. *Chem. Phys.* **1994**, *189*, 315.

(32) Thoma, A.; Wurfel, B. E.; Schlachta, R.; Lask, G. M.; Bondybey, V. E. A pulsed discharge source of transients for matrix isolation spectroscopy. *J. Phys. Chem.* **1992**, *96*(18), 7231.

(33) Prengel, A. T.; Dehaven, J.; Johnson, E. J.; Davidovits, P. Production of neutral atoms by pulsed laser heating. *J. Appl. Phys.* **1977**, *48*, 3551.

(34) Downer, M. C.; Fork, R. L.; Shank, C. V. Femtosecond imaging of melting and evaporation at a photoexcited silicon surface. *J. Opt. Soc. Am.* **1985**, *B2*, 595.

(35) Heimbrook, L. A.; Rasanen, M.; Bondybey, V. E. Production of clusters by laser vaporization and their trapping in rare gas matrices. *J. Phys. Chem.* **1987**, *91*, 2468.

(36) Knight, L. B., Jr. Production methods for ESR studies of neutral and charged radicals. In *Chemistry and Physics of Matrix-Isolated Species*; Andrews, L., Moskovits, M., Eds.; North Holland: Amsterdam, 1989; p 167.

(37) Knight, L. B., Jr.; Earl, E.; Ligon, A. R.; Cobranchi, D. P.; Woodward, J. R.; Bostick, J. M. ; Davidson, E. R.; Feller, D. Neon matrix ESR and CI theoretical investigation of AlF$^+$; photoionization of AlF from thermal and laser sputtering generation methods. *J. Am. Chem. Soc.* **1986**, *108*, 5065.

(38) Knight, L. B., Jr.; Gregory, B. W.; Cobranchi, S. T.; Feller, D.; Davidson, E. R. Laser sputtering generation of B$_2$ for ESR matrix isolation studies: comparison with ab initio CI theoretical calculations. *J. Am. Chem. Soc.* **1987**, *109*, 3521.

(39) Knight, L. B., Jr.; Ligon, A.; Cobranchi, S. T.; Cobranchi, D. P.; Earl, E.; Feller, D.; Davidson, E. R. Neon matrix ESR and CI theoretical investigation of ^{10}BF$^+$ and ^{11}BF$^+$: Photoionization of BF from reactive laser sputtering and high temperature sources. *J. Chem. Phys.* **1986**, *85*, 5437.

(40) Knight, L. B., Jr.; Cobranchi, S. T.; Petty, J. T.; Earl, E. Electron spin resonance investigations of ^{11}B^{12}C, ^{11}B^{13}C, and ^{10}B^{12}C in neon, argon, and krypton matrices at 4 K: Comparison with theoretical results. *J. Chem. Phys.* **1989**, *90*(2), 690.

(41) Knight, L. B., Jr.; McKinley, A. J.; Babb, R. M.; Morse, M. D.; Arrington, C. A. Laser vaporization electron generation of the SiB and SiAl radicals for matrix isolation electron spin resonance studies; comparison with theoretical calculations and assignment of their electronic ground states as X$^4\Sigma$. *J. Chem. Phys.* **1993**, *98*, 6749.

(42) Knight, L. B., Jr.; Hill, D. W.; Kirk, T. J.; Arrington, C. A. Matrix isolation ESR and theoretical investigation of ^{11}B^{14}N^{11}B and ^{10}B^{14}N^{11}B - laser vaporization generation. *J. Phys. Chem.* **1992**, *96*, 555.

(43) Presilla-Marquez, J. D.; Gay, S. C.; Rittby, C. M. L.; Graham, W. R. M. Vibrational spectra of tetra-atomic silicon-carbon clusters ii. Si$_2$ C$_2$ in ar at 10 K. *J. Chem. Phys.* **1995**, *102*, 6354.

(44) Kranze, R. H.; Withey, P. A.; Rittby, C. M. L.; Graham, W. R. M. Fourier transform infrared observation of the ν_9 stretching mode of linear C$_9$ in Ar at 10 K. *J. Chem. Phys.* **1995**, *103*, 6841.

(45) Chertihin, G. V.; Andrews, L. Reactions of laser-ablated Zr and Hf atoms with hydrogen - matrix infrared spectra of the MH, MH$_2$, MH$_3$, and MH$_4$ molecules. *J. Phys. Chem.* **1995**, *99*(41), 15004.

(46) Greene, T. M.; Brown, W.; Andrews, L.; Downs, A. J.; Chertihin, G. V.; Runeberg, N.; Pyykko, P. Matrix infrared spectroscopic and ab initio studies of ZnH$_2$, CdH$_2$ and related metal hydride species. *J. Phys. Chem.* **1995**, *99*(20), 7925.

(47) Tague, T. J.; Andrews, L. Reactions of pulsed-laser evaporated boron atoms with hydrogen—infrared spectra of boron hydride intermediate species in solid argon. *J. Am. Chem. Soc.* **1994**, *116*(11), 4970.

(48) Burkholder, T. R.; Andrews, L. Reactions of boron atoms with molecular oxygen—infrared spectra of BO, BO$_2$, B$_2$ O$_2$, B$_2$ O$_3$, and BO$_2^-$ in solid argon. *J. Chem. Phys.* **1991**, *95*(12), 8697.

(49) Andrews, L.; Hassanzadeh, P.; Burkholder, T. R.; Martin, J. M. L. Reactions of pulsed laser produced boron atoms and nitrogen atoms in a condensing argon stream. *J. Chem. Phys.* **1993**, *98*(2), 922.

(50) Burkholder, T. R.; Andrews, L. Reactions of boron atoms with CO—matrix infrared spectra of BCO, (BCO)$_2$, and B(CO)$_2$. *J. Phys. Chem.* **1992**, *96*(25), 10195.

(51) Hassanzadeh, P.; Andrews, L. Reaction of halogens with laser-ablated boron - infrared spectra of BX$_n$ (X=F,Cl,Br,I; n=1,2,3) in solid argon. *J. Phys. Chem.* **1993**, *97*(19), 4910.

(52) Andrews, L.; Burkholder, T. R. Infrared spectra of boron atom-water molecule reaction products trapped in solid argon. *J. Phys. Chem.* **1991**, *95*(22), 8554.

(53) Burkholder, T. R.; Andrews, L.; Bartlett, R. J. Reactions of boron atoms with carbon dioxide—matrix and ab initio calculated infrared spectra of OBCO. *J. Phys. Chem.* **1993**, *97*(14), 3500.

(54) Hassanzadeh, P.; Andrews, L.; Davy, R. D. Laser ablated boron atom reaction with carbon disulfide - infrared spectrum of SBCS in solid argon and ab initio geometry and frequency calculations for possible products. *J. Phys. Chem.* **1993**, *97*(29), 7412.

(55) Hassanzadeh, P.; Andrews, L. Reactions of pulsed laser evaporated boron atoms with methane 1. Synthesis and characterization of a novel molecule with carbon boron double bond - HBCBH. *J. Am. Chem. Soc.* **1992**, *114*(23), 9239.

(56) Hassanzadeh, P.; Hannachi, Y.; Andrews, L. Pulsed laser evaporated boron atom reactions with methane 2. Infrared spectra of H$_2$ CBH$_2$, H$_2$ CBH, HCBH, and HBCBH in solid argon. *J. Phys. Chem.* **1993**, *97*(24), 6418.

(57) Hannachi, Y.; Hassanzadeh, P.; Andrews, L. Ab initio study of the insertion product of the boron methane reaction - CH$_3$ BH. *J. Phys. Chem.* **1994**, *98*(28), 6950.

(58) Andrews, L.; Hassanzadeh, P.; Martin, J. M. L; Taylor, P. R. Pulsed laser evaporated boron atom reactions with acetylene - infrared spectra and quantum chemical structure and frequency calculations for several novel BC$_2$ H$_2$ and HBC$_2$ molecules. *J. Phys. Chem.* **1993**, *97*(22), 5839.

(59) Martin, J. M. L.; Taylor, P. R.; Hassanzadeh, P.; Andrews, L. Boron atom reactions with acetylene - ab initio calculated and observed isotopic infrared spectra of the borirene radical BC$_2$ H$_2$ - a fingerprint match. *J. Am. Chem. Soc.* **1993**, *115*(6), 2510.

(60) Thompson, C. A.; Andrews, L.; Martin, J. M. L.; Elyazal, J. Infrared spectra of boron atom-ammonia reaction products in solid argon. *J. Phys. Chem.* **1995**, *99*(38), 13839.

(61) Thompson, C. A.; Andrews, L. Reactions of B atoms with NH$_3$ to produce HBNH, BNBH, and B$_2$ N. *J. Am. Chem. Soc.* **1995**, *117*, 10125.

(62) Burkholder, T. R.; Andrews, L. Matrix infrared detection of OBSO. *Chem. Phys. Lett.* **1992**, *199*(5), 455.

(63) Weltner, W., Jr.; Van Zee, R. J. Carbon molecules, ions, and clusters. *Chem. Rev.*, 89(8), 1713 and references therein.

(64) Weltner, W., Jr.; Van Zee, R. J.; Li, S. Magnetic molecules in matrices. *J. Phys. Chem.* **1995**, *99*(17), 6277.

(65) Li, S.; Van Zee, J.; Weltner, W., Jr. Magneto-infrared spectra of the Si$_2$, Ge$_2$, and Sn$_2$ molecules in rare-gas matrices. *J. Chem. Phys.* **1994**, *100*(10), 7079.

(66) Hamrick, Y. M.; Van Zee, R. J.; Weltner, W., Jr. Electron spin resonance of the boron trimer. *J. Chem. Phys.* **1991**, *95*, 3009.

(67) Hamrick, Y. M.; Van Zee, R. J.; Weltner, W., Jr. Electron spin resonance and ground states of the boron and aluminum trimers. *J. Chem. Phys.* **1992**, *96*(3), 1767.

(68) Van Zee, R. J.; Li, S.; Weltner, W., Jr. Hyperfine interaction and structure of a gallium arsenide cluster—$Ga_2 As_3$. *J. Chem. Phys.* **1993**, *98*(6), 4335.

(69) Van Zee, R. J.; Weltner, W., Jr. Cu_7 cluster—pentagonal bipyramid. *J. Chem. Phys.* **1990**, *92*(11), 6976.

(70) Li, S.; Van Zee, R. J.; Weltner, W., Jr.; Raghavachari, K. Si_3-Si_7 - experimental and theoretical infrared spectra. *Chem. Phys. Lett.* **1995**, *243*(3−4), 275.

(71) Honea, E. C.; Ogura, A.; Murray, C. A.; Raghavachari, K.; Sprenger, W. O.; Jarrold, M. F.; Brown, W. L. Raman spectra of size-selected silicon clusters and comparison with calculated structures. *Nature* **1993**, *366*, 42.

(72) Moerner, W. E.; Basché, T. Optical spectroscopy of single impurity molecules in solids. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 457.

(73) Moerner, W. E. Examining nanoenvironments in solids on the scale of a single, isolated impurity molecule. *Science* **1994**, *265*, 46.

(74) Forney, D.;Althaus, H.; Maier, J. P. An electronic absorption spectrum of C_2^+: $B^4\Sigma_u^- \leftarrow X^4\Sigma_g^-$. *J. Phys. Chem.* **1987**, *91*, 6458.

(75) Rasanen, M.; Liu, J. Y.; Dzugan, T. P.; Bondybey, V. E. Matrix studies of the products of laser vaporization of graphite. *Chem. Phys. Lett.* **1987**, *142*(5), 308.

(76) Fernando, W. T. M. L.; O'Brien, L. C.; Bernath, P. F. Fourier transform emission spectroscopy: The $B^4\Sigma^- - X^4\Sigma^-$ transition of BC. *J. Chem. Phys.* **1990**, *93*, 8482.

(77) Douglas, A. E. ; Herzberg, G. *Can. J. Res. A*, **1940**, *18*, 179.

(78) Mosher, O. A.; Frosch, R. P. Experimental identification of the ground state of BN in a rare-gas matrix. *J. Chem. Phys.* **1970**, *52*(11), 5781.

(79) Bredohl, H.; Dubois, I.; Houbrechts, Y.; Nzohabonayo, P. The singlet bands of BN. *J. Phys. B: Atom. Mol. Phys.* **1984**, *17*, 95.

(80) Martin, J. M. L.; Lee, T. J.; Scuseria, G. E.; Taylor, P. R. Ab initio multireference study of the BN molecule. *J. Chem. Phys.* **1992**, *97*, 6549.

(81) Peterson, K. A. Accurate multireference configuration interaction calculations on the lowest $^1\Sigma^+$ and $^3\Pi$ electronic states of C_2, CN^+, BN and BO^+. *J. Chem. Phys.* **1995**, *102*, 262.

(82) Hirsch, G.; Buenker, R. J. Theoretical study of the properties of BC and its positive ion in their ground and excited electronic states. *J. Chem. Phys.* **1987**, *87*(10), 6004.

(83) Nosanow, L. H. Theory of quantum crystals. *Phys. Rev.* **1966**, *146*, 120.

(84) Bauer, H.; Beau, M.; Bernhardt, A.; Friedl, B.; Reyher, H. J. Implantation of atoms in liquid helium for the purpose of impurity spectroscopy. *Phys. Lett. A* **1989**, *137*, 217.

(85) Arndt, M.; Kanorsky, S. I.; Weis, A.; Hänsch, T. W. Can paramagnetic atoms in superfluid helium be used to search for permanent electric dipole moments. *Phys. Lett. A* **1993**, *174*, 298.

(86) Fujisaki, A.; Sano, K.; Kinoshta, T.; Takahashi, Y.; Yabuzabi, T. Implantation of neutal atoms into liquid helium by laser sputtering. *Phys. Rev. Lett.* **1993**, *71*, 1039.

(87) Kanorsky, S. I.; Arndt, M.; Dziewior, R.; Weis, A.; Hänsch, T. W. Pressure shift and broadening of the resonance line of barium atoms in liquid helium. *Phys. Rev. B* **1994**, *50*, 6296.

(88) Goodman, J.; Brus, L. E. Rydberg states in condensed phases: Evidence for small "bubble" formation around NO 3sσ ($a^2\Sigma^+$) in solid rare gases. *J. Chem. Phys.* **1977**, *67*, 933.

(89) Goodman, J.; Brus, L. E. Vibrational relaxation and small "bubble" spectroscopy of the NO 3sσ ($a^2\Sigma^+$) rydberg state in solid rare gases. *J. Chem. Phys.* **1978**, *69*, 4083.

(90) Chergui, M.; Schwentner, N.; Chandrasekharan, V. Rydberg fluorescence of NO trapped in rare gas matrices. *J. Chem. Phys.* **1988**, *89*(3), 1277.

(91) Stangassinger, A.; Mane, I.; Bondybey, V. E. UV electronic spectra and structure of thallium-rare gas complexes. *Chem. Phys.* **1995**, *201*, 227.

(92) Luo, F.; McBane, G. C.; Kim, G.; Giese, C. F.; Gentry, W. R. The weakest bond: Experimental observation of helium dimer. *J. Chem. Phys.* **1993**, *98*, 3564.

(93) Lewerenz, M.; Schilling, B.; Toennies, J. P. A new scattering deflection method for determining and selecting the sizes of large liquid clusters of ^{4} He. *Chem. Phys. Lett.* **1993**, *206*, 381.

(94) Scheidemann, A.; Schilling, B.; Toennies, J. P. Capture of foreign atoms by helium clusters. *Physica B* **1990**, *165*, 135.

(95) Lewerenz, M.; Schilling, B.; Toennies, J. P. Successive capture and coagulation of atoms and molecules to small cluster in large liquid helium clusters. *J. Chem. Phys.* **1995**, *102*, 8191.

(96) Goyal, S.; Schutt, D. L.; Scoles, G. Infrared spectroscopy in highly quantum matrices: vibrational spectrum of $(SF_6)_{n=1,2}$ attached to helium clusters. *J. Phys. Chem.* **1993**, *97*, 2236.

(97) Frötenicht, R.; Toennies, J. P.; Vilesov, A. High-resolution infrared spectroscopy of SF_6 embedded in He clusters. *Chem. Phys. Lett.* **1994**, *229*, 1.

(98) Hartmann, M.; Miller, R. E.; Toennies, J. P.; Vilesov, A. Rotationally resolved spectrosopy of SF_6 in liquid helium clusters —a molecular probe of cluster temperature. *Phys. Rev. Lett.* **1995**, *75*, 1566.

(99) Hartmann, M.; Miller, R. E.; Toennies, J. P.; Vilesov, A. Liquid helium droplets—a gentle matrix for ultracold, high resolution molecular spectroscopy. *Science* **1996**, in press.

(100) Brink, D. M.; Stringari, S. *Z. Phys. D* **1990**, *15*, 257.

(101) Stienkemeier, F.; Ernst, W. E.; Higgins, J.; Scoles, G. On the use of liquid helium cluster beams for the preparation and spectrosopy of the triplet states of alkali dimers and other weakly bound complexes. *J. Chem. Phys.* **1995**, *102*, 615.

(102) Stienkemeier, F.; Higgins, J.; Ernst, W. E.; Scoles, G. Laser spectroscopy of alkali-doped helium clusters. *Phys. Rev. Lett.* **1995**, *74*, 3592.

(103) Boltnev, R. E.; Gordon, E. B.; Khmelenko, V. V.; Krushinskaya, I. N.; Martynenko, M. V.; Pelmenev, A. A.; Popov, E. A.; Shestakov, A. F. Luminescence of nitrogen and neon atoms isolated in solid helium. *Chem. Phys.* **1994**, *189*(2), 367.

(104) Meyer, H. What causes the observed differences between solid H_2 and D_2. *Physica B*, **1994**, *197*, 13.

(105) Silvera, I. F. The solid molecular hydrogens in the condensed phase: Fundamentals and static properties. *Rev. Mod. Phys.* **1980**, *52*, 393.

(106) Fajardo, M. E.; Tam, S.; Thompson, T. L.; Cordonnier, M. E. Spectroscopy and reactive dynamics of atoms trapped in molecular hydrogen matrices. *Chem. Phys.* **1994**, *189*(2), 351.

(107) Fajardo, M. E. Matrix isolation spectroscopy of metal atoms generated by laser ablation. ii. the Li/Ne, Li/D_2 and Li/H_2 systems. *J. Chem. Phys.* **1993**, *98*(1), 110.

(108) Danilychev, A. V.; Bondybey, V. E.; Apkarian, V. A.; Tanaka, S.; Kajihara, H.; Koda, S. Photodynamics in oxygen doped solid deuterium. *J. Chem. Phys.* **1995**, *103*, 4292.

(109) Jacox, M. E. The vibrational energy levels of small transient molecules isolated in neon and argon matrices. *Chem. Phys.* **1994**, *189*(2), 149.

(110) Jacox, M. E. Comparison of the electronic levels of diatomic molecules in the gas phase and in inert solid matrices. *J. Mol. Struct.* **1987**, *157*, 43−59.

(111) Jacox, M. E. Comparison of the ground state vibrational fundamentals of diatomic molecules in the gas phase and in inert solid matrices. *J. Mol. Spectrosc.* **1985**, *113*, 286.

(112) Knight, L. B., Jr. ESR investigations of molecular cation radicals in neon matrices at 4 K: Generation, trapping; ion-neutral reactions. *Acc. Chem. Res.* **1986**, *19*, 313.

(113) Miller, T. A., Bondybey, V. E., Eds. *Molecular Ions: Spectroscopy, Structure and Chemistry*; North Holland: Amsterdam, 1983.

(114) Jacox, M. E.; Thompson, W. E. The production and spectroscopy of molecular ions isolated in solid neon. *Res. Chem. Intermed.* **1989**, *12*(1), 33.

(115) Bondybey, V. E.; Miller, T. A.; English, J. H. Electronic absorption spectra of molecular cations. *J. Chem. Phys.* **1980**, *72*, 2193.

(116) Rossetti, R.; Brus, L. E. Waveguide propagation in frozen gas matrices. *Rev. Sci. Instrum.* **1980**, *51*(4), 467.

(117) Jacox, M. E. Matrix-isolation study of the products of the interaction between metastable Ar and Kr atoms and chloroform. Photodecomposition of $HCCl_2^+$ and $HCCl_2^-$. *Chem. Phys.* **1976**, *12*, 51.

(118) Wight, Ch. A.; Ault, B. S.; Andrews, L. On microwave discharge sources of new chemical species for matrix-isolation spectroscopy and the identification of charged species. *J. Chem. Phys.* **1976**, *65*(4), 1244.

(119) Prochaska, F. T.; Andrews, L. Matrix photodissociation and photoionization of carbon tetrahalides with noble gas resonance irradiation. *J. Chem. Phys.* **1977**, *67*(3), 1091.

(120) Gasyna, Z.; Andrews, L.; Schatz, P. N. Near-infrared absorption spectra of C_{60} radical cations and anions prepared simultaneously in solid argon. *J. Phys. Chem.* **1992**, *96*(4), 1525.

(121) Knight, L. B., Jr.; Steadman, J. An experimental procedure for ESR studies of rare gas matrix isolated cation radicals: $^{12}CO^+$, $^{13}CO^+$, $^{14}NH_3^+$, and $^{15}NH_3^+$. *J. Chem. Phys.* **1982**, *77*(4), 1750.

(122) Knight, L. B., Jr.; Kerr, K.; Villanueva, M.; McKinley, A. J. Theoretical and neon matrix electron spin resonance studies of the methanol cation: CH_3OH^+, CH_3OD^+, CH_2DOH^+, and $^{13}CH_3$-OH^+. *J. Chem. Phys.* **1992**, *97*(8), 5363.

(123) Engelking, P. C. Corona excited supersonic expansion. *Rev. Sci. Instrum.* **1986**, *57*(9), 2274.

(124) Engelking, P. C. Spectroscopy of jet-cooled ions and radicals. *Chem. Rev.* **1991**, *91*, 399.

(125) Bai, H.; Ault, B. S. Coupling of a corona discharge to matrix isolation for the production of intermediates: The CCl_4 system. *Chem. Phys. Lett.* **1992**, *188*(1,2), 126.

(126) Szczepanski, J.; Personette, W.; Vala, M. Pulsed-glow discharge/matrix isolation method for the production and trapping of organic ions: application to para-dimethoxybenzene. *Chem. Phys. Lett.* **1991**, *185*(3,4), 324.

(127) Weltner, W., Jr. *Magnetic Atoms and Molecules*; Van Nostrand: Reinhold, New York, 1983.

(128) Reents, W. D.; Bondybey, V. E. Fourier-transform mass spectroscopic studies of ionized atoms and clusters produced by laser vaporization of metals and semiconductors. *Chem. Phys. Lett.* **1986**, *125*, 324.

(129) Knight, L. B., Jr.; Herlong, J. O.; Babb, R.; Earl, E.; Hill, D. W.; Arrington, C. A. Matrix isolation electron spin resonance studies of $^{28,28}Si_2^+$, $^{28,29}Si_2^+$, $^{29,29}Si_2^+$, Ge_2^+, and $^{73}Ge_2^+$ produced by pulsed

laser vaporization. Comparison with theoretical calculations. *J. Phys. Chem.* **1991**, *95*(7), 2732.

(130) Knight, L. B., Jr.; Petty, J. T. Neon matrix ESR investigation of $^{69,71}GaAs^+$ generated by the photoionization of laser vaporized GaAs(s). *J. Chem. Phys.* **1988**, *88*(1), 481.

(131) Knight, L. B., Jr.; Herlong, J. O. Laser vaporization generation of $^{69}Ga^{31}P^+$ and $^{71}Ga^{31}P^+$ for neon matrix electron spin resonance studies: Electronic structure comparison with $GaAs^+$. *J. Chem. Phys.* **1989**, *91*(1), 69.

(132) McKinley, A. J.; Michl. J. EPR-ENDOR spectroscopy of matrix-isolated NH_3^+ and CH_3 radicals. *J. Phys. Chem.* **1991**, *95*(7), 2674.

(133) Van Zee, R. J.; Weltner, W., Jr. ESR spectra of the Cu_2^+, Ag_2^+, and Au_2^+ ions. *Chem. Phys. Lett.* **1989**, *162*(6), 437.

(134) Cheeseman, M.; Van Zee, R. J.; Flanagan, H. L.; Weltner, W., Jr. Transition-metal diatomics: Mn_2, Mn_2^+, CrMn. *J. Chem. Phys.* **1990**, *92*(3), 1553.

(135) Van Zee, R. J.; Hamrick, Y. M.; Li, S.; Weltner, W., Jr. ESR of Co, Rh, Ir trimers and diatomic ions. *Chem. Phys. Lett.* **1992**, *195*(2,3), 214.

(136) Van Zee, R. J.; Li, S.; Weltner, W., Jr. Ground state electronic states of ZrO^+, HfO^+, and Nb_2^+. ESR spectra of matrix-isolated ions. *Chem. Phys. Lett.* **1994**, *217*(4), 381.

(137) Kasai, P. H. $Na^0(epoxy)_{1-3}$ complexes and dissociative electron capture of the epoxy system: Matrix isolation ESR study. *J. Am. Chem. Soc.* **1990**, *112*(11), 4313.

(138) Kasai, P. H. Dissociative electron capture of propylene oxide: Matrix isolation ESR study. *J. Am. Chem. Soc.* **1991**, *113*(5), 1539.

(139) Kasai, P. H. Dissociative electron capture of sulfones and sulfonates: Matrix isolation ESR study. *J. Am. Chem. Soc.* **1991**, *113*(9), 3317.

(140) Kasai, P. H. Succinimidyl and phthalimidyl radicals: Matrix isolation ESR study. *J. Am. Chem. Soc.* **1992**, *114*(8), 2875.

(141) Hacker, N. P.; Kasai, P. H. Dissociative electron capture of diazoquinones: Matrix isolation ESR study. *J. Am. Chem. Soc.* **1993**, *115*(13), 5410.

(142) Köppe, R.; Kasai, P. H. ESR spectra, structure and photochemistry of carboxylic acid and ester anions: matrix isolation study. *Chem. Phys.* **1994**, *189*(2), 401.

(143) Köppe, R.; Kasai, P. H. Aliphatic ketone anion-radicals: A matrix isolation ESR study. *J. Phys. Chem.* **1994**, *98*(49), 12904.

(144) Jacox, M. E.; Thompson, W. E. The vibrational spectra of molecular ions isolated in solid neon. I. CO_2^+ and CO_2^-. *J. Chem. Phys.* **1989**, *91*(3), 1410.

(145) Thompson, W. E.; Jacox, M. E. The vibrational spectra of molecular ions isolated in solid neon. VII. CO^+, $C_2O_2^+$, and $C_2O_2^-$. *J. Chem. Phys.* **1991**, *95*(2), 735.

(146) Forney, D.; Thompson, W. E.; Jacox, M. E. The vibrational spectra of molecular ions isolated in solid neon. IX. HCN^+, HNC^+, and CN^-. *J. Chem. Phys.* **1992**, *97*(3), 1664.

(147) Jacox, M. E.; Thompson, W. E. The vibrational spectra of molecular ions isolated in solid neon. IV. NO^+, NO^-, $ONNO^+$, and $ONNO^-$. *J. Chem. Phys.* **1990**, *93*(11), 7609.

(148) Strobel, A.; Knobloch, N.; Agreiter, J.; Smith, A. M.; Niedner-Schatteburg, G.; Bondybey, V. E. Identification, structure, and vibrational assignment of the NO dimer cation. *J. Phys. Chem.* **1995**, *99*(3), 872.

(149) Herbig, G. H. The diffuse interstellar bands. IV region 4400−6850 Å. *Astrophys. J.* **1975**, *196*, 129.

(150) Herbig, G. H.; Leka, K. D. The diffuse interstellar bands. VIII. New features between 6000 and 8650 Å. *Astrophys. J.* **1991**, *382*, 193.

(151) Joblin, C.; Maillard, J. P.; d'Hendecourt, L.; Léger, A. Detection of diffuse interstellar bands in the infrared. *Nature* **1990**, *346*, 729.

(152) Salama, F.; Allamandola, L. J. Electronic absorption spectroscopy of matrix-isolated polycyclic aromatic hydrocarbon cations. I. The naphthalene cation ($C_{10}H_8^+$). *J. Chem. Phys.* **1991**, *94*(11), 6964.

(153) Salama, F.; Joblin, C.; Allamandola, L. J. Electronic absorption spectroscopy of matrix-isolated polycyclic aromatic hydrocarbon cations. II. The phenanthrene cation ($C_4H_{10}^+$) and its 1-methyl-derivative. *J. Chem. Phys.* **1994**, *101*(12), 10252.

(154) Hudgins, D. M., S. A. Sandford; Allamandola, L. J. Infrared spectroscopy of polycyclic aromatic hydrocarbon cations. 1. Matrix-Isolated naphtalene and perdeuterated naphthalene. *J. Phys. Chem.* **1994**, *98*(16), 4243.

(155) Hudgins, D. M. and Allamandola, L. J. Infrared spectroscopy of matrix-isolated polycyclic aromatic hydrocarbon cations. 2. The members of the thermodynamically most favorable series through coronene. *J. Phys. Chem.* **1995**, *99*(10), 3033.

(156) Hudgins, D. M.; Allamandola, L. J. Infrared spectroscopy of matrix-isolated polycyclic aromatic hydrocarbon cations. 3. The polyacenes anthracene, tetracene, and pentacene. *J. Phys. Chem.* **1995**, *99*(22), 8978.

(157) Joblin, C.; d'Hendecourt, L.; Léger, A.; Défouneau, D. Infrared spectroscopy of gas-phase PAH molecules. 1. Role of the physical environment. *Astron. Astrophys.* **1994**, *281*, 923.

(158) Joblin, C.; Boissel, P.; Léger, A.; d'Hendecourt, L.; Défourneau, D. Infrared spectroscopy of gas-phase PAH molecules. II. Role of the temperature. *Astron. Astrophys.* **1995**, *299*(3), 835.

(159) Szczepanski, J.; Personette, W.; Pellow, R.; Chandrasekhar, T. M.; Roser, D.; Cory, M.; Zerner, M.; Vala, M. Vibrational and electronic spectra of matrix-isolated para-dichlorobenzene radical cations. *J. Chem. Phys.* **1992**, *96*(1), 35.

(160) Szczepanski, J.; Vala, M.; Talbi, D.; Parisel, O.; Ellinger, Y. Electronic and vibrational spectra of matrix isolated anthracene radical cations: Experimental and theoretical aspects. *J. Chem. Phys.* **1993**, *98*(6), 4494.

(161) Szczepanski, J.; Wehlburg, Ch.; Vala, M. Vibrational and electronic spectra of matrix-isolated pentacene cations and anions. *Chem. Phys. Lett.* **1995**, *232*, 221.

(162) Thaddeus, P.; Gottlieb, C. A.; Mollaaghababa, R.; Vrtilek, J. M. Free carbenes in the interstellar gas. *J. Chem. Soc., Faraday Trans.* **1993**, *89*(13), 2125.

(163) Thaddeus, P. In *Molecules and Grains in Space*; Nenner, I., Brechignac, P., Eds.; American Institute of Physics: New York, 1994.

(164) Fulara, J.; Lessen, D.; Freivogel, P.; Maier, J. P. Laboratory evidence for highly unsaturated hydrocarbons as carriers of some of the diffuse interstellar bands. *Nature* **1993**, *366*, 439.

(165) Freivogel, P.; Fulara, J.; Maier, J. P. Highly unsaturated hydrocarbons as potential carriers of some diffuse interstellar bands. *Astrophys. J.* **1994**, 431.

(166) Freivogel, P.; Fulara, J.; Jakobi, M.; Forney, D.; Maier, J. P. Electronic absorption spectra of linear carbon chains in neon matrices. II. C_{2n}^-, C_{2n}, and $C_{2n}H$. *J. Chem. Phys.* **1995**, *103*(1), 54.

(167) Smith, A. M.; Agreiter, J.; Bondybey, V. E. The laser induced fluorescence of $C_{10}H_2^+$. In preparation.

(168) Agreiter, J.; Smith, A. M.; Härtle, M.; Bondybey, V. E. Laser-induced fluorescence of matrix-isolated $C_4N_2^+$. *Chem. Phys. Lett.* **1994**, *225*(1−3), 87.

(169) Agreiter, J.; Smith, A. M.; Bondybey, V. E. Laser-induced fluorescence of matrix-isolated $C_6N_2^+$ and of $C_8N_2^+$. *Chem. Phys. Lett.* **1995**, *241*, 317.

(170) Smith, A. M.; Agreiter, J.; Bondybey, V. E. Laser-induced fluorescence of matrix-isolated $H{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{\equiv}N^+$ and $H{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{\equiv}C{-}C{\equiv}N^+$. *Chem. Phys. Lett.* **1995**, *244*(5,6), 379.

(171) Fayet, P.; Wöste, L. Production and study of metal cluster ions. *Surf. Sci.* **1984**, *156*, 134.

(172) Fayet, P.; Wöste, L. Experiments on size-selected metal cluster ions in a triple quadrupole arrangement. *Z. Phys. D* **1986**, *3*, 177.

(173) Rivoal, J. C.; Grisolia, C.; Lignieres, J.; Kreisle, D.; Fayet, P.; Wöste, L. Absorption spectroscopy of size-selected trimers and pentamers transition metal clusters isolated in rare gas solids: Preliminary steps. *Z. Phys. D* **1989**, *12*, 481.

(174) Lindsay, D. M.; Meyer, F.; Harbich, W. Neutralization and matrix deposition experiments on mass-selected silver atoms and clusters. *Z. Phys. D* **1989**, *12*, 15.

(175) Harbich, W.; Fedrigo, S.; Meyer, F.; Lindsay, D. M.; Lignieres, J.; Rivoal, J. C.; Kreisle, D. Deposition of mass selected silver clusters in rare gas matrices. *J. Chem. Phys.* **1990**, *93*(12), 8535.

(176) Fedrigo, S.; Harbich, W.; Buttet, J. Optical response of Ag_2, Ag_3, Au_2 and Au_3 in argon matrices. *J. Chem. Phys.* **1993**, *99*(8), 5712.

(177) Fedrigo, S.; Harbich, W.; Buttet, J. Collective dipole oscillations in small silver clusters embedded in rare-gas matrices. *Phys. Rev. B* **1993**, *47*(16), 47.

(178) Hu, Z.; Shen, B.; Zhou, Q.; Deosaran, S.; Lombardi, J. R.; Lindsay, D. M.; Harbich, W. Raman spectra of mass-selected vanadium dimers in argon matrices. *J. Chem. Phys.* **1991**, *95*(3), 2206.

(179) Hu, Z.; Dong, J.-G.; Lombardi, J. R.; Lindsay, D. M. Raman spectra of mass-selected dihafnium in argon matrices. *J. Phys. Chem.* **1993**, *97*(37), 9263.

(180) Hu, Z.; Dong, J.-G.; Lombardi, J. R.; Lindsay, D. M. Optical and raman spectroscopy of mass-selected tungsten dimers in argon matrices. *J. Chem. Phys.* **1992**, *97*(11), 8811.

(181) Dong, J.-G.; Hu, Z.; Craig, R.; Lombardi, J. R.; Lindsay, D. M. Raman spectra of mass-selected cobalt dimers in argon matrices. *J. Chem. Phys.* **1994**, *101*(11), 9280.

(182) Haouari, H.; Wang, H.; Craig, R.; Lombardi, J. R.; Lindsay, D. M. Resonance raman spectrum and excitation profile of mass-selected zirconium trimers. *J. Chem. Phys.* **1995**, *103*(22), 9527.

(183) Hu, Z.; Shen, B.; Lombardi, J. R.; Lindsay, D. M. Spectroscopy of mass-selected tantalum dimers in argon matrices. *J. Chem. Phys.* **1992**, *96*(12), 8757.

(184) Wang, H.; Craig, R.; Haouari, H.; Dong, J.-G.; Hu, Z.; Vivoni, A.; Lombardi, J. R.; Lindsay, D. M. Absorption and raman spectroscopy of mass-selected tantalum tetramers in argon matrices. *J. Chem. Phys.* **1995**, *103*(9), 3289.

(185) Gilbert, J. R.; Leroi, G. E.; Allison, J. Modified residual gas analyser as source of mass-selected ion beams. *Int. J. Mass Spectrom. Ion Processes* **1991**, *107*, 247.

(186) Sabo, M. S.; Allison, J.; Gilbert, J. R.; Leroi, G. E. Bridging the gap between what mass spectrometrists want and what spectroscopists can do: An instrument for spectroscopic investigation of matrix-isolated, mass-selected ions. *Appl. Spectrosc.* **1991**, *45*(4), 535.

(187) Halasinski, T. M.; Godbout, J. T.; Allison, J.; Leroi, G. E. Infrared detection of matrix-isolated, mass-selected ions. *J. Phys. Chem.* **1994**, *98*(15), 3930.

(188) Godbout, J. T.; Halasinski, T. M.; Leroi, G. E.; Allison, J. Matrix isolation of mass-selected cations: Are counterions present and how are they formed? *J. Phys. Chem.* **1996**, *100*, 2892−2899.

(189) Forney, D.; Jakobi, M.; Maier, J. P. Matrix absorption spectroscopy on mass-selected ions. *Faraday Discuss. Chem. Soc.* **1988**, *86*, 96.

(190) Forney, D.; Jakobi, M.; Maier, J. P. Absorption spectroscopy of mass-selected ions in neon matrices. *J. Chem. Phys.* **1989**, *90*(1), 600.

(191) Freivogel, P.; Fulara, J.; Lessen, D.; Forney, D.; Maier, J. P. Absorption spectra of conjugated hydrocarbon cations chains in neon matrices. *Chem. Phys.* **1994**, *189*(2), 335.

(192) Forney, D.; Freivogel, P.; Fulara, J.; Maier, J. P. Electronic absorption spectra of cyano-substituted polyacetylene cations in neon matrices. *J. Chem. Phys.* **1995**, *102*(4), 1510.

(193) Forney, D.; Fulara, J.; Freivogel, P.; Jakobi, M.; Lessen, D.; Maier, J. P. Electronic absorption spectra of linear carbon chains in neon matrices. I. C_6^-, C_6, and C_6H. *J. Chem. Phys.* **1995**, *103*(1), 48.

(194) Fulara, J.; Freivogel, P.; Forney, D.; Maier, J. P. Electronic absorption spectra of linear carbon chains in neon matrices. III. $HC_{2n+1}H$. *J. Chem. Phys.* **1995**, *103*(20), 8805.

(195) Bondybey, V. E.; Sears, T. J.; English, J. H.; Miller, T. A. Low temperature gas phase and matrix studies of the $C_6H_3F_3^+$ and $C_6H_3Cl_3^+$ radical cations. *J. Chem. Phys.* **1980**, *73*, 2063.

(196) Ellis, H. B., Jr.; Ellison, G. B. Photoelectron spectroscopy of HNO^- and DNO^-. *J. Chem. Phys.* **1983**, *78*(11), 6541.

(197) Alton, G. D.; McConnell, J. W. The emittances and brightnesses of high-intensity negative ion sources. *Nucl. Instrum. Methods Phys. Res. A* **1988**, *268*, 445.

(198) Middleton, R.; Klein, J.; Fink, D. A CO_2 negative ion source for ^{14}C dating. *Nucl. Instrum. Methods Phys. Res. B* **1989**, *43*, 231.

(199) Barger, R. L.; Broida, H. P. Spectra of C_3 in solidified gases at 4 K and 20 K. *J. Chem. Phys.* **1965**, *43*, 2364.

(200) Weltner, W., Jr,; McLeod, D., Jr. Spectroscopy of carbon vapor condensed in rare-gas matrices at 4 K. iii. *J. Chem. Phys.* **1966**, *45*(8), 3096.

(201) Milligan, D. E.; Jacox, M. E.; Abouaf-Marguin, L. Vacuum-ultraviolet photolysis of acetylene in inert matrices. spectroscopic study of the species C_2. *J. Chem. Phys.* **1967**, *46*(12), 4562.

(202) Graham, W. R. M.; Dismuke, K. I.; Weltner, W. The C_4 molecule. *Astrophys. J.* **1976**, *204*, 301.

(203) Szczepanski, J.; Vala, M. Correlation of infrared and uv-visible bands of matrix-isolated carbon clusters. *J. Phys. Chem.* **1991**, *95*, 2792.

(204) Van Zee, R. J.; Li, S.; Weltner, W., Jr. Gd_2—the highest spin diatomic molecule. *J. Chem. Phys.* **1994**, *100*(5), 4010.

(205) Brabson, G. D.; Andrews, L. Infrared and visible spectra of small selenium clusters (n=2,3,4) in solid argon. *J. Phys. Chem.* **1992**, *96*(23), 9172.

(206) Li, S.; Van Zee, R. J.; Weltner, W., Jr. Fourier-transform infrared magneto-optical spectra of the Se_2, TeSe, and Te_2 molecules in rare-gas matrices at 4K. *J. Chem. Phys.* **1993**, *99*(1), 762.

(207) Knight, L. B., Jr.; Cobranchi, S. T.; Herlong, J. O.; Arrington, C. A. Laser vaporization generation of $Al^{12}C$, $Al^{13}C$, $Al^{12}C_2$, and $Al^{13}C_2$ for rare gas matrix electron spin resonance studies: experimental-theoretical comparisons. *J. Chem. Phys.* **1990**, *92*(10), 5856.

(208) Knight, L. B., Jr.; Babb, R.; Hill, D. W.; McKinley, A. J. Laser vaporization generation of the diatomic radicals PdB, ^{105}PDB, PdAl, and $^{105}PdAl$—electron spin resonance investigation in neon matrices at 4 K. *J. Chem. Phys.* **1992**, *97*(5), 2987.

(209) Van Zee, R. J.; Li, S.; Weltner, W., Jr. TiNb, ZrNb, and HfV molecules—ESR, ground states, and isovalency. *J. Chem. Phys.* **1995**, *103*(7), 2762.

(210) Hamrick, Y. M.; Van Zee, R. J.; Weltner, W., Jr. ESR of bimetallic transition-metal molecules—Mo and W with Cu, Ag, and Au. *Chem. Phys. Lett.* **1991**, *181*, 193.

(211) Cheeseman, M.; Van Zee, R. J.; Weltner, W., Jr. ESR spectrum and ground state of the ScCr molecule. *J. Phys. Chem.* **1990**, *94*(20), 7808.

(212) Van Zee, R. J.; Li, S.; Hamrick, Y. M.; Weltner, W., Jr. Electron-spin resonance of the Co, Rh, and Ir dihydride molecules. *J. Chem. Phys.* **1992**, *97*(11), 8123.

(213) Van Zee, R. J.; Hamrick, Y. M.; Li, S.; Weltner, W., Jr. Cobalt, rhodium, and iridium dioxide molecules and walsh-type rules. *J. Phys. Chem.* **1992**, *96*(18), 7247.

(214) Hamrick, Y. M.; Van Zee, R. J.; Godbout, J. T.; Weltner, W., Jr.; Lauderdale, W. J.; Stanton, J. F.; Bartlett, R. J. The BCO molecule. *J. Phys. Chem.* **1991**, *95*(7), 2840; erratum **1991**, *95*(13), 5366.

(215) Knight, L. B., Jr.; Herlong, J. O.; Kirk, T. J.; Arrington, C. A. Laser vaporization generation of $B^{14}NH$,$B^{15}NH$, $B^{14}ND$, $B^{16}O$ and $B^{17}O$—electron spin resonance investigation in neon matrices under ultrcold trapping conditions. *J. Chem. Phys.* **1992**, *96*(8), 5604.

(216) Van Zee, R. J.; Li, S.; Weltner, W., Jr. V, Nb, and Ta hydride molecules in deuterium and rare-gas matrices—infrared and electron spin resonance spectra. *J. Chem. Phys.* **1995**, *102*(11), 4367.

(217) Knight, L. B., Jr.; Herlong, J. O.; Cobranchi, S. T.; Kirk, T. Laser vaporization generation of $PdCH_3$,$^{105}PdCH_3$, and $Pd^{13}CH_3$ for electron spin resonance neon matrix study at 4 K. *J. Chem. Phys.* **1990**, *92*(11), 6463.

(218) Knight, L. B., Jr.; Jones, G. C.; King, G. M.; Babb, R. M. et al. Electron spin resonance and theoretical studies of the PO_2 and AsO_2 radicals in neon matrices at 4 K - laser vaporization and x-irradiation radical generation techniques. *J. Chem. Phys.* **1995**, *103*(2), 497.

(219) Knight, L. B., Jr.; McKinley, A. J.; Babb, R. M.; Hill, D. W. et al. Electron spin resonance investigation of Sc_2^+ in neon matrices and assignment of its ground electronic state as $X^4\Sigma$—comparison with theoretical calculations. *J. Chem. Phys.* **1993**, *99*(10), 7376.

(220) Li, S.; Van Zee, R. J.; Weltner, W., Jr. Infrared spectra of the GeSi and SnSi molecules in argon matrices. *Chem. Phys. Lett.* **1994**, *229*(4−5), 531.

(221) Li, S.; Van Zee, R. J.; Weltner, W., Jr. Far-infrared spectra of small gallium phosphide, arsenide, and antimonide molecules in rare-gas matrices at 4 K. *J. Phys. Chem.* **1993**, *97*(44), 11393.

(222) Li, S.; Van Zee, J.; Weltner, W., Jr. Infrared spectra of InP, InAs, and InSb molecules in rare-gas matrices at 4 K: Magnetic effects. *J. Phys. Chem.* **1994**, *98*(9), 2275.

(223) Martin, J. M. L.; Taylor, P. R.; Yustein, J. T.; Burkholder, T. R.; Andrews, L. Pulsed laser vaporization of boron/carbon pellets: Infrared spectra and quantum chemical structures and frequencies for BC_2. *J. Chem. Phys.* **1993**, *99*(1), 12.

(224) Chertihin, G. V.; Andrews, L. Reactions of laser ablated Ti atoms with hydrogen during condensation in excess argon—infrared spectra of the TiH, TiH_2, TiH_3, and TiH_4 molecules. *J. Am. Chem. Soc.* **1994**, *116*(18), 8322.

(225) Andersson, K. The electronic spectrum of Cr_2. *Chem. Phys. Lett.* **1995**, *237*, 212.

(226) Thompson, C. A.; Andrews, L.; Davy, R. D. Reactions of beryllium species with N_2—infrared spectra and quantum chemical calculations of beryllium dinitrogen complexes in solid argon and nitrogen. *J. Phys. Chem.* **1995**, *99*(20), 7913.

(227) Anderson, D. T.; Winn, J. S. Matrix isolated HF: the high resolution infrared spectrum of a cryogenically solvated hindered rotor. *Chem. Phys.* **1994**, *189*(2), 171.

(228) Thompson, C. A.; Andrews, L. Reactions of laser ablated be atoms with O_2: Infrared spectra of beryllium oxides in solid argon. *J. Chem. Phys.* **1994**, *100*(12), 8689.

(229) Tague, T. J.; Andrews, L. Reactions of beryllium atoms with hydrogen—matrix infrared spectra of novel product molecules. *J. Am. Chem. Soc.* **1993**, *115*(25), 12111.

(230) Chertihin, G. V.; Andrews, L. Infrared spectra of FeH, FeH_2, and FeH_3 in solid argon. *J. Phys. Chem.* **1995**, *99*(32), 12131.

(231) Knight, L. B., Jr.; Cleveland, C. B.; Frey, R. F.; Davidson, E. R. Electron spin resonance investigation of small magnesium cluster cation radicals, Mg_n^+, in neon and argon matrices at 4 K—comparison with ab initio calculations. *J. Chem. Phys.* **1994**, *100*(11), 7867.

(232) Knight, L. B., Jr.; Babb, R. M.; King, G. M.; McKinley, A. J.; Morse, M. D.; Arrington, C. A. Laser vaporization generation of $Y^{10}B^+$, $Y^{11}B^+$, and YAl^+ for electron spin resonance studies in neon matrices at 4 K: Comparison with theoretical results. *J. Chem. Phys.* **1993**, *98*(6), 4404.

(233) Knight, L. B., Jr.; Cobranchi, S. T.; Herlong, J.; Kirk, T. et al. Laser vaporization rare gas matrix-isolation electron spin resonance studies of PdH_2^+, PdD_2^+, PdH, and PdD—theoretical investigation of PdH_2^+. *J. Chem. Phys.* **1990**, *92*(5), 2721.

(234) James, A. M.; Kowalczyk, P.; Fournier, R.; Sinard, B. Electronic spectroscopy of the niobium dimer molecule: Experimental and theoretical results. *J. Chem. Phys.* **1993**, *99*, 8504.

(235) Sinard, B.; James, A. M.; Kowalczyk, P.; Fournier, R.; Hackett, P. A. High resolution spectroscopy of small transition metal molecules. Recent experimental and theoretical progress on group v diatomics. *Proc. SPIE*, 1994.

(236) Agreiter, J.; Lorenz, M.; Smith, A. M.; Bondybey, V. E. Spectroscopy and isotope selective fluorescence of BO_2 in solid neon. In preparation, 1996.

CR940262H