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Laser and Fourier Transform Spectroscopy of Novel Propellant Molecules

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13. ABSTRACT (MAXIMUM 200 WORDS)

A wide variety of molecules were studied by the techniques of Fourier transform spectroscopy and visible laser spectroscopy. Molecules studied include CCN, CaBH$_4$, CH$_3$N, CN, IF, ICl, IBr, BC, CH, CH, C$_2$, C$_3$, C$_{60}$, LiF, AlF, AlCl, HF, HCl, B3F$_2$, BiH, AlH, BaH, and GaH. These molecules were detected by infrared, visible and ultraviolet emission and absorption measurements.

14. SUBJECT TERMS
visible; Fourier transform; spectroscopy; ultraviolet; laser; UV/VIS; interhalogen(s); metal(s); borohydrides; C$_2$; C$_3$; C$_{60}$; dihalide(s); methyl nitrene; dicarbon nitride; CH; CCN

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A. Introduction.

The goal of our work is the study of the spectroscopy and chemistry of a variety of energetic molecules. They have been studied by high resolution infrared and visible Fourier transform spectroscopy as well as visible laser spectroscopy. Many of these molecules such as C_2, BC, BH and AlH may prove to be useful in boosting the specific impulse of the H_2/O_2 propellant system if they are trapped in solid hydrogen. Some of the molecules studied such as CH, CN, AlF, HCl, HF and AlCl are of interest in the modelling of current conventional aluminized propellants. Some of our work also has applications in the simulation of rocket plume signatures and in the Air Force chemical laser program.

B. Dicarbon Nitride, CCN.

The ultracold emission spectrum of CCN was observed with an Engelking-type [Engelking, *Rev. Sci. Instrum.* 57, 2274 (1986)] free radical jet expansion source. The precursor diazoacetonitrile $HC(N_2)CN$ was seeded in He and discharged to provide CCN. The observation[1] of the 000-000, 000-001, 000-002 and 000-100 vibronic bands of the $\tilde{A}^2\Delta$ - $\tilde{X}^2\Pi$ transition allowed the accurate determination of the ν_1 (1923.255 cm^{-1}), ν_3 (1050.764 cm^{-1}) and $2\nu_2$ (2094.816 cm^{-1}) vibrational frequencies. The very precise wavenumber scale of the Fourier transform spectrometer allows these infrared active vibrational modes to be determined from an electronic emission spectrum. Electronic emission spectra of ultracold free radicals detected by Fourier transform spectroscopy is a powerful technique for the studying of transient molecules.

C. Metal Borohydrides, $CaBH_4$, $SrBH_4$, $LiBH_4$ and $NaBH_4$.

Ca and Sr vapors react spontaneously with diborane (B_2H_6) to give $CaBH_4$ and $SrBH_4$ free radicals[2]. We have detected the $\tilde{B}^2E$ - $\tilde{X}^2A_1$ and $\tilde{A}^2A_1$ - $\tilde{X}^2A_1$ electronic transitions by low resolution laser-induced fluorescence. Some preliminary infrared emission experiments on $LiBH_4$

and $NaBH_4$ suggest that they can be vaporized in a furnace. The infrared spectra were very complex and there was considerable decomposition of the heated $LiBH_4$ and $NaBH_4$ solids.

D. Methyl Nitrene, CH_3N.

The near ultraviolet emission spectrum of methyl nitrene, CH_3N, was observed at a resolution of 0.07 cm^{-1} with a Fourier transform spectrometer. The $\tilde{A}^3E - \tilde{X}^3A_2$ system of CH_3N (analagous to the $A^3\Pi - X^3\Sigma^-$ system of NH) was rotationally analysed. The CH_3N molecule was made in an Engelking jet source using CH_3N_3 as the precursor. Our rotational constants were consistent with a short C-N bond length of 1.420 Å. This short bond length was not predicted by the early ab initio calculations but is in agreement with the most recent results of H.F. Schaefer's group [Y. Xie et al. *J. Am. Chem. Soc.* **111**, 5181 (1989)].

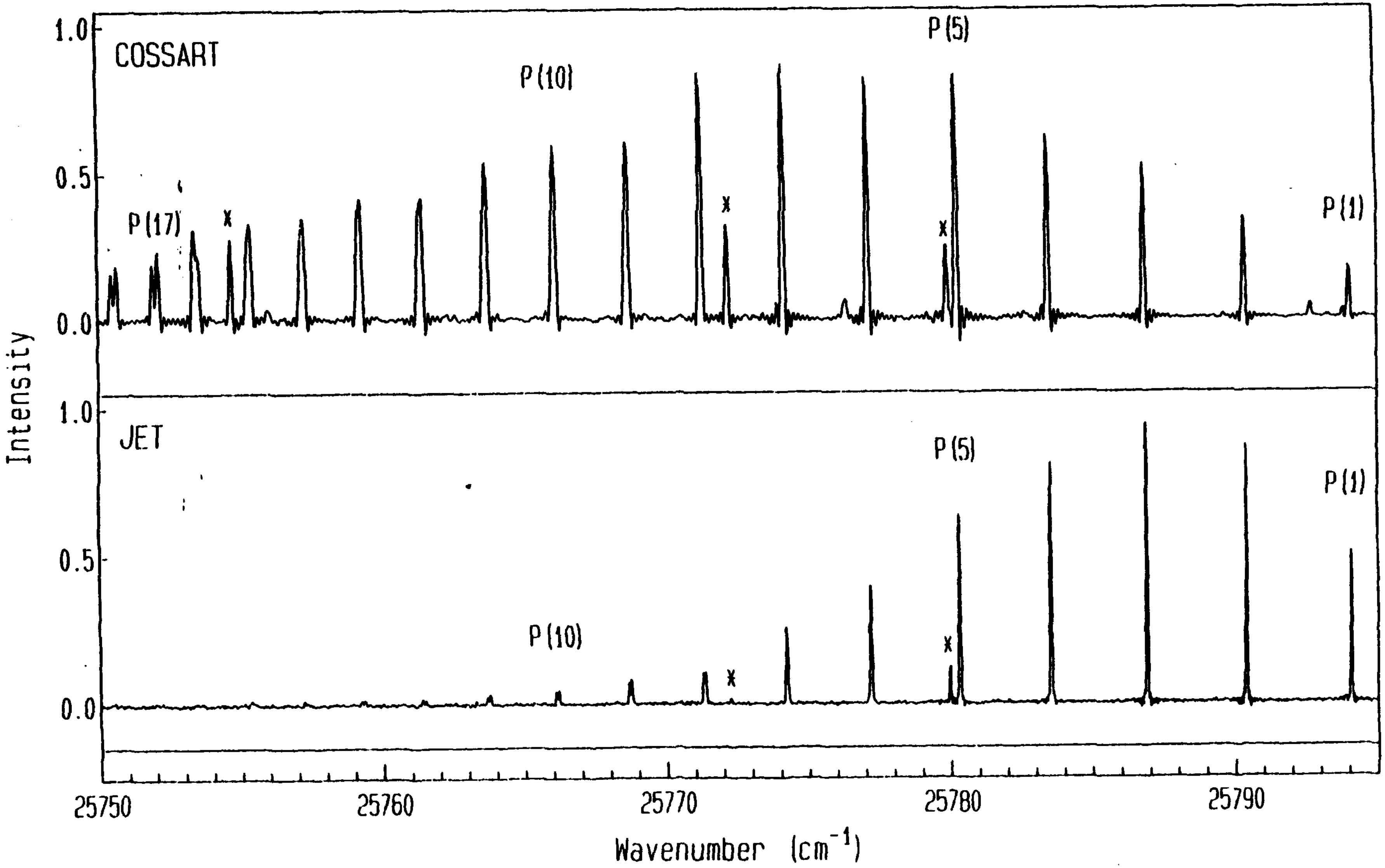
E. Cyanogen, CN.

In the same experiments which provided the CCN and CH_3N spectra, new spectra of CN were observed. Both the $B^2\Sigma^+ - X^2\Sigma^+$ transition[4] (violet system) and the $A^2\Pi - X^2\Sigma^+$ transition[5] (red system) were observed. These spectra were rotationally cold but vibrationally hot. The great simplification provided by the jet source compared to a conventional discharge is illustrated in Figure 1. The analysis of numerous vibrational bands allowed new potential energy curves to be calculated. These curves (Figure 2) extend to high v and are very useful for the calculation of the spectral and thermochemical properties of CN in high temperature environments. The CN molecule is an important free radical in the combustion of conventional propellants.

F. Review Articles.

Two review articles were published on the research supported by our Air Force contract. A review of the high resolution infrared spectra of transient molecules was published in the

Figure 1: The 0-0 band of the $B^2\Sigma^+ - X^2\Sigma^+$ transition of CN observed at room temperature (Cossart, top) and 90K (jet, bottom).



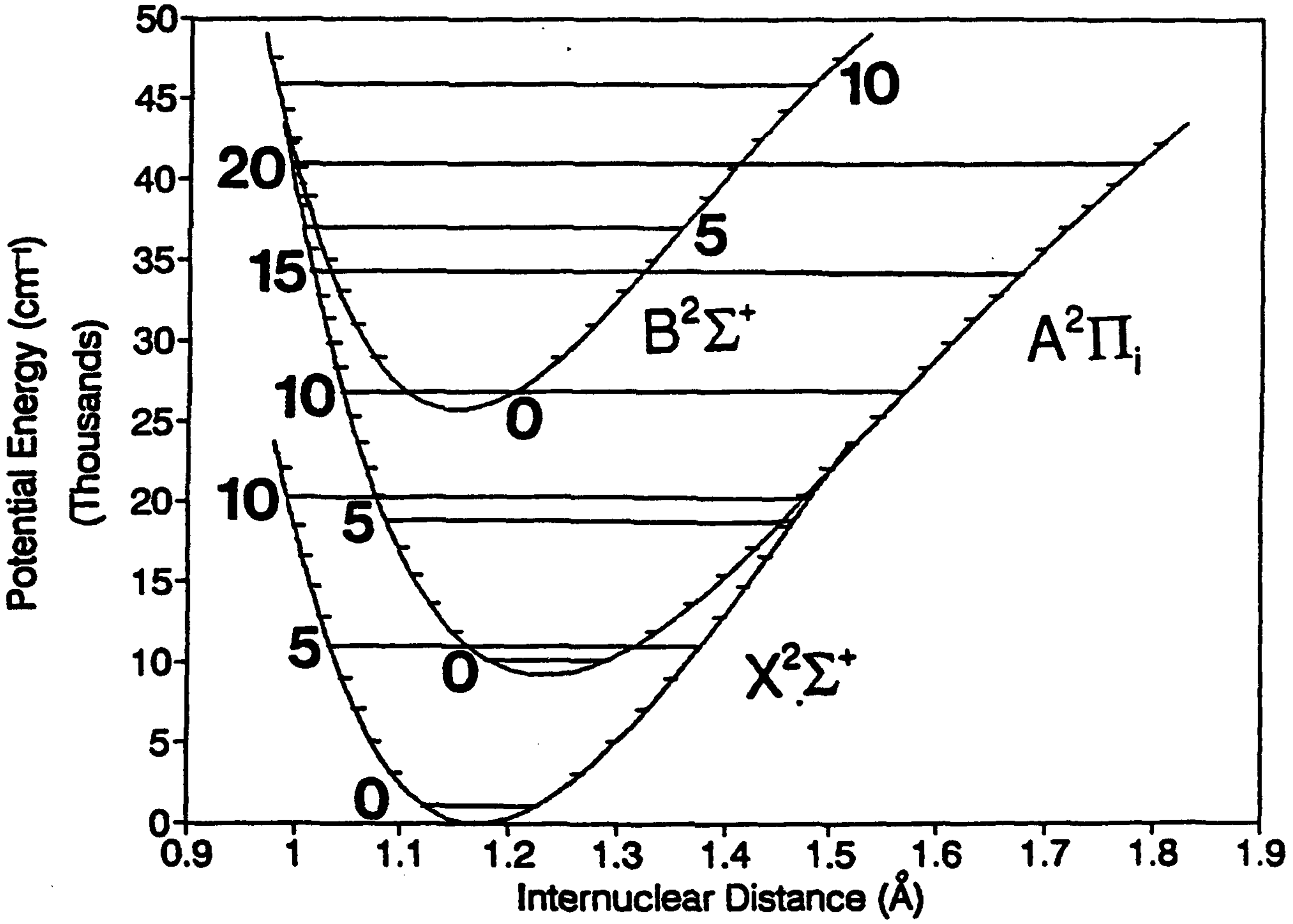


Figure 2: The RKR potential energy curves of the $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ electronic states of CN.

Annual Review of Physical Chemistry[6]. While a review of our organometallic research on molecules such as $CaBH_4$ was published in Science magazine[7].

G. Interhalogens, IF, ICl and IBr.

The vibration-rotation spectra of IF,[8], ICl [9] and IBr [10] were recorded. Interhalogens are not of direct interest to the HEDM program (except as oxidizers), but they are important to the Air Force chemical laser program. We recorded the ICl and IBr spectra to test the far infrared performance of our new Bruker Fourier transform spectrometer. Surprisingly no high resolution vibration-rotation spectra of ICl and IBr were available in the literature prior to our work. The band origins at 384 cm^{-1} for ICl and 267 cm^{-1} for IBr are in the far infrared where conventional spectrometers have difficulty operating.

H. Boron-Containing Molecules, BC, BH and BD.

The BC molecule was discovered[11] by detection of the $B^4\Sigma^- - X^4\Sigma^-$ transition in a composite wall (B_4C/Cu) hollow cathode sputter source. The electronic emission of BC near 5590 Å was recorded with the Kitt Peak Fourier transform spectrometer. As a bonus, the same spectra contained the $A^1\Pi - X^1\Sigma^+$ transition of BH. By adding D_2 to the source, the corresponding transition of BD was observed for both ^{10}B and ^{11}B isotopes.[12] The BC and BH molecules are both important high energy density materials (HEDM) since they yield (P. Carrick, private communication) a substantial improvement in the specific impulse (I_{sp}) of the hydrogen/oxygen system if they are trapped in solid hydrogen.

I. CH.

New emission measurements of the $A^2\Delta - X^2\Pi$ and $B^2\Sigma^- - X^2\Pi$ electronic transitions as well as the infrared vibration-rotation transitions were recorded as impurities in spectra recorded for other purposes. A simultaneous analysis of all available data[13] has resulted in a greatly improved set of molecular constants for CH. The CH molecule, like BH, is potential additive to solid hydrogen. In addition CH is a key free radical when any hydrocarbons (i.e. conventional fuels) are burned. Our new constants in the ground state cover the high-J and high-v levels necessary for simulations of the hot CH molecule during the combustion of propellants.

J. Pure Carbon Molecules, C_2, C_3 and C_{60}.

Pure carbon molecules continue to fascinate the scientific community. Although C_{60} is too stable to be useful a high energy density material, C_2, C_3 and smaller clusters are more relevant. For instance, C_2 and C_3 can be synthesized by trapping carbon atoms in solid hydrogen. The accidental or intentional agglomeration of the C atoms leads to C_2 and C_3.

A new metastable state of C_3 ($\tilde{a}^3\Pi_u$) was discovered by observing the $\tilde{b}^3\Pi_g$ - $\tilde{a}^3\Pi_u$ electronic transition in the infrared.[14] The infrared transition of C_3 was detected near 6500 cm^{-1} in emission from a microwave discharge of hydrocarbons. The same transition was also seen in absorption with a diode laser since the lower $\tilde{a}^3\Pi_u$ state has a long lifetime (20 ms in an argon matrix).

For C_{60} the gas-phase vibration-rotation bands were also seen in emission by vaporizing a sample of C_{60}. The hot C_{60} vapor showed[15] the four infrared active bands expected on the basis of the previous solid state infrared work. This work demonstrates that our favourite technique of infrared emission spectroscopy also works well for large molecules in which the rotational structure is not resolved.

In the same Fourier transform spectra that yielded data for CH_3N, CCN and CN molecules, the C_2 Swan system, $d^3\Pi_g$ - $a^3\Pi_u$, was also identified. As for CN, the use of the

Engelking jet source gave vibrationally hot but rotationally cold (90 K) spectra. These data were combined with some additional laser data taken from the literature to provide greatly improved constants for the Swan system of C_2. Like CH and CN, C_2 is always present during the combustion of conventional propellants and is a potential HEDM molecule.

K. Metal Halides, LiF, AlF and AlCl.

We have found high resolution vibration-rotation emission spectroscopy to be a powerful tool for the spectroscopic characterization of high temperature materials. This technique has received little attention at long wavelengths (greater than 5 microns). If lithium or aluminum compounds are used as propellants with an oxidizer containing fluorine or chlorine then LiF, AlF and AlCl will be among the exhaust products. We have recorded the vibration-rotation emission spectra of LiF [16] and AlF [17] near 900 cm^{-1} as well as AlCl [18] near 500 cm^{-1}. The quality of the spectra is illustrated (Figure 3) with a section of the AlCl spectrum near the 2-1 band head. Our data on AlCl has already been used to simulate the AlCl features detected in a rocket plume in the ultraviolet (J. Drakes, Arnold AFB, private communication).

L. Hydrogen Halides, HF and HCl.

During the course of our work with light metal halides, we observed the pure rotational emission spectra of hot HF[19,20] and hot HCl[20]. Our emission technique is thus useful for infrared electronic spectra (e.g. C_3) infrared vibration-rotation spectra of small molecules (e.g. AlH) as well as large molecules (e.g. C_{60}) and for the pure rotation spectra of small molecules (e.g. HCl). Indeed we find it to be the technique of choice for high temperature systems in general.

The vibration-rotation emission spectra of hot HCl and hot HF were recorded by the pyrolysis of the freon CHF_2Cl at 1000°C. Surprisingly the high-J and high-v transitions of HCl

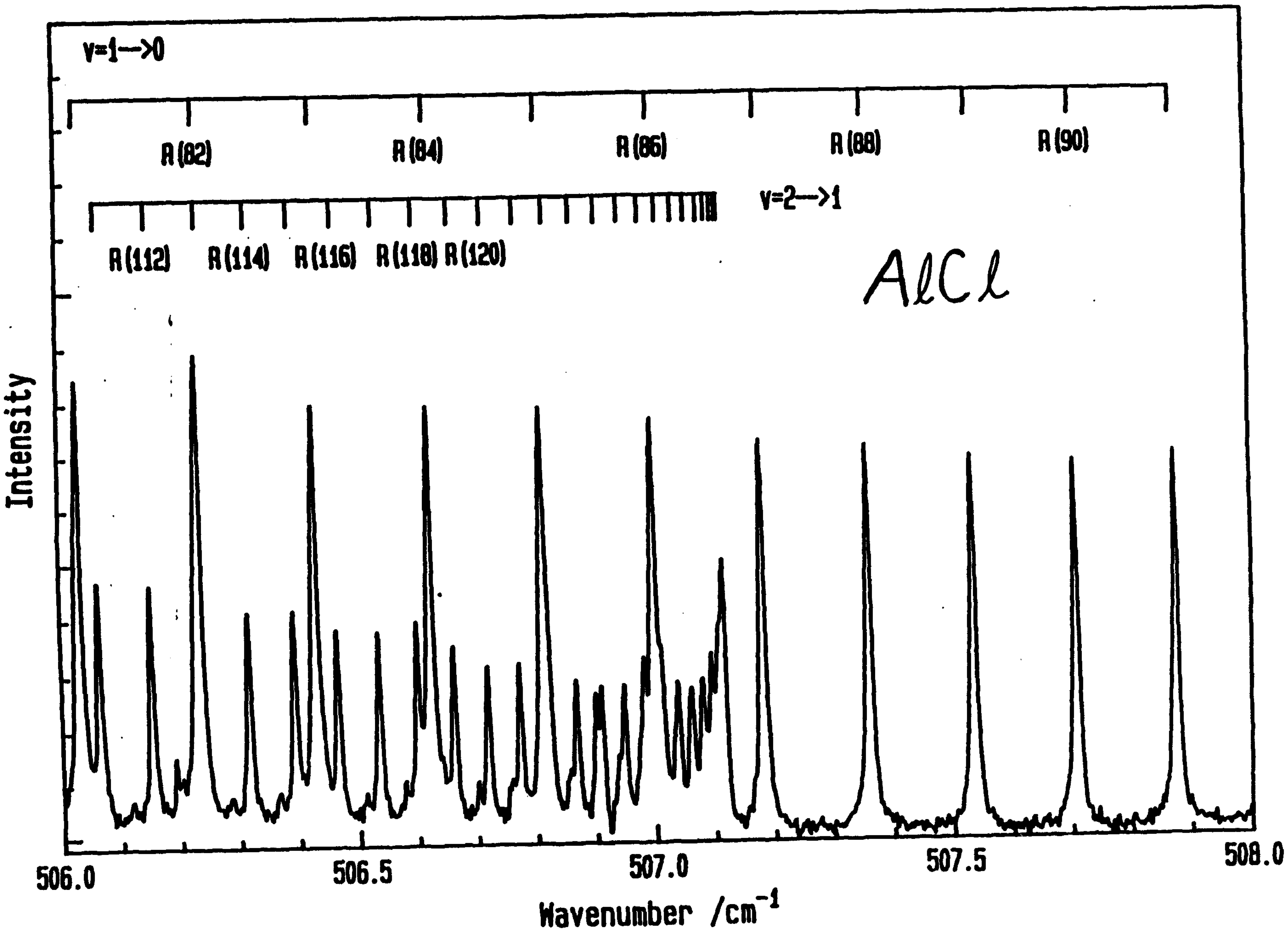


Figure 3: The vibration-rotation emission spectrum of AlCl.

and HF were poorly known before our work. We measured these lines to a precision of better than ± 0.0002 cm^{-1}. These data are very useful for the simulation of the spectra of exhaust plumes of any propellant containing chlorine or fluorine.

M. Beryllium Difluoride, BeF_2.

The technique of infrared emission spectroscopy can also be applied to polyatomic molecules such as BeF_2. If Be is used as an additive to boost the performance of a propellant for space-based applications, then BeF_2 will be an exhaust product with fluorine oxidizers. We recorded the vibration-rotation emission spectrum[21] of the antisymmetric stretching mode near 1550 cm^{-1}. The fundamental and numerous hot bands were analysed and an equilibrium molecular structure was determined [r_e(Be-F) = 1.372971Å]. This work is the first complete analysis of a metal dihalide spectrum.

N. Metal Hydrides and Deuterides, BiH, BiD, AlH, AlD, BaH, GaH and GaD.

Our infrared emission work was extended to metal hydrides by observing BiH [22], BiD [22] and BaH [23]. For technical reasons (ease of handling and favorable chemistry) we chose to start with Bi and Ba metals. When these experiments were successful we began a series of experiments on the Al + H_2 system.

Molten aluminum is very corrosive and we had some initial difficulties with the destruction of our furnace tubes. The solution to our materials problem was to use a carbon liner for our tube furnace. In this way we could operate up to 1600°C without difficulty. Excellent spectra of AlH (Figure 4 and 5) were recorded[24]. No evidence for the formation of AlH_2 could be found in our spectra.

We have also begun to develop new data reduction techniques. In order to derive the best Al-H interaction potential we fitted our data directly to the eigenvalues of the appropriate Schrödinger equation with a parameterized potential ("inverse perturbation approach"). For our potential we used an extension of the modified Morse function suggested by Coxon [J. Coxon et al., Can J. Phys. 70, 40 (1992)]. The results of our fit are illustrated in Figure 6. This potential reproduces the experimental data available for the lower half of the well and is qualitatively correct for the upper half where only ab initio data (points in Figure 6) are available. These potentials are necessary to simulate the interaction of aluminum with hydrogen in an advanced propellant. In order to test our theoretical approach some spectra[25] of GaH and GaD were also recorded.

O. Conclusion and Future Directions

The techniques of laser and Fourier transform spectroscopy are able to characterize energetic molecules suitable as propellants. Infrared emission spectroscopy of high temperature molecules has proved to be a particularly useful technique. The molecules of interest can be made by a variety of techniques including electrical discharges and high temperature vaporization and reaction.

The performance of a potential propellant depends both on the reaction exothermicity and the molecular weight of the product molecules. Light elements are most suitable so that we have concentrated our work on elements such as Li, Be, B and Al. We believe that simple thermal evaporation in a high temperature furnace followed by a chemical reaction and deposition into a solid hydrogen matrix holds considerable promise as a scheme to increase the performance of the hydrogen/oxygen system. We recommend the study of the reactions of laser and thermally

Fig. 4 - Overview Emission Spectrum Of AlH

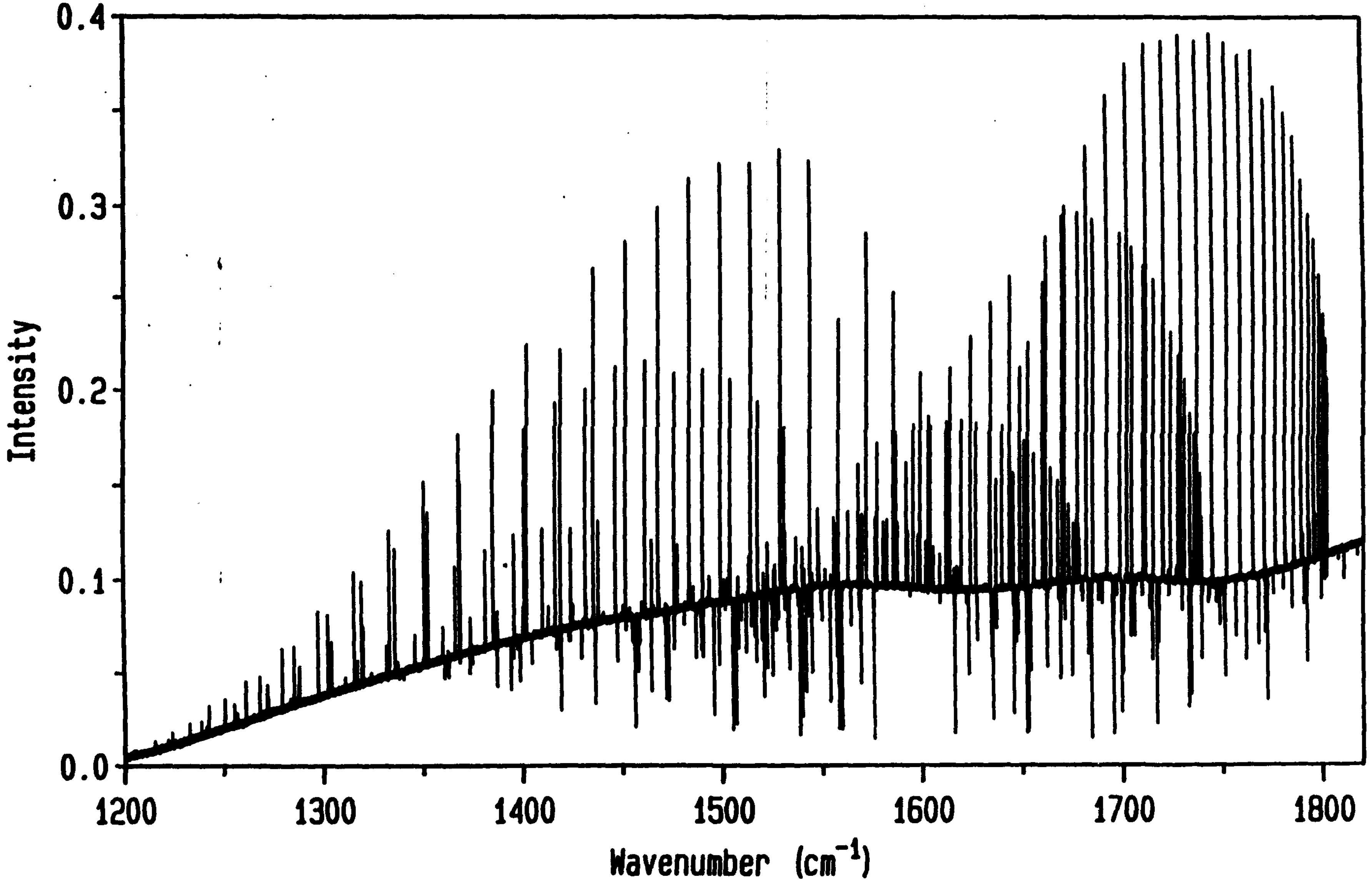


Fig. 5 - Band Head Of The Fundamental Band Of AlH

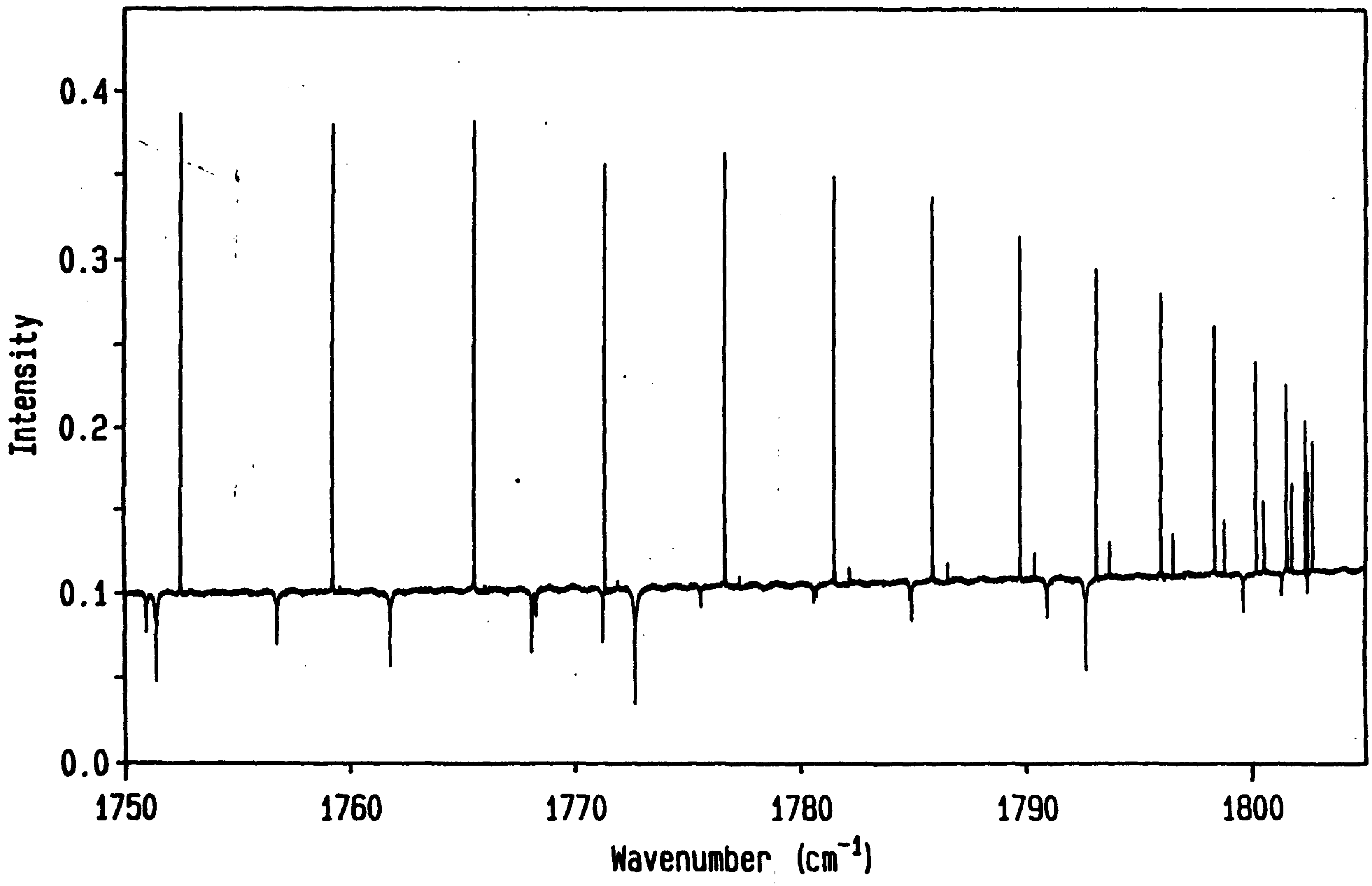
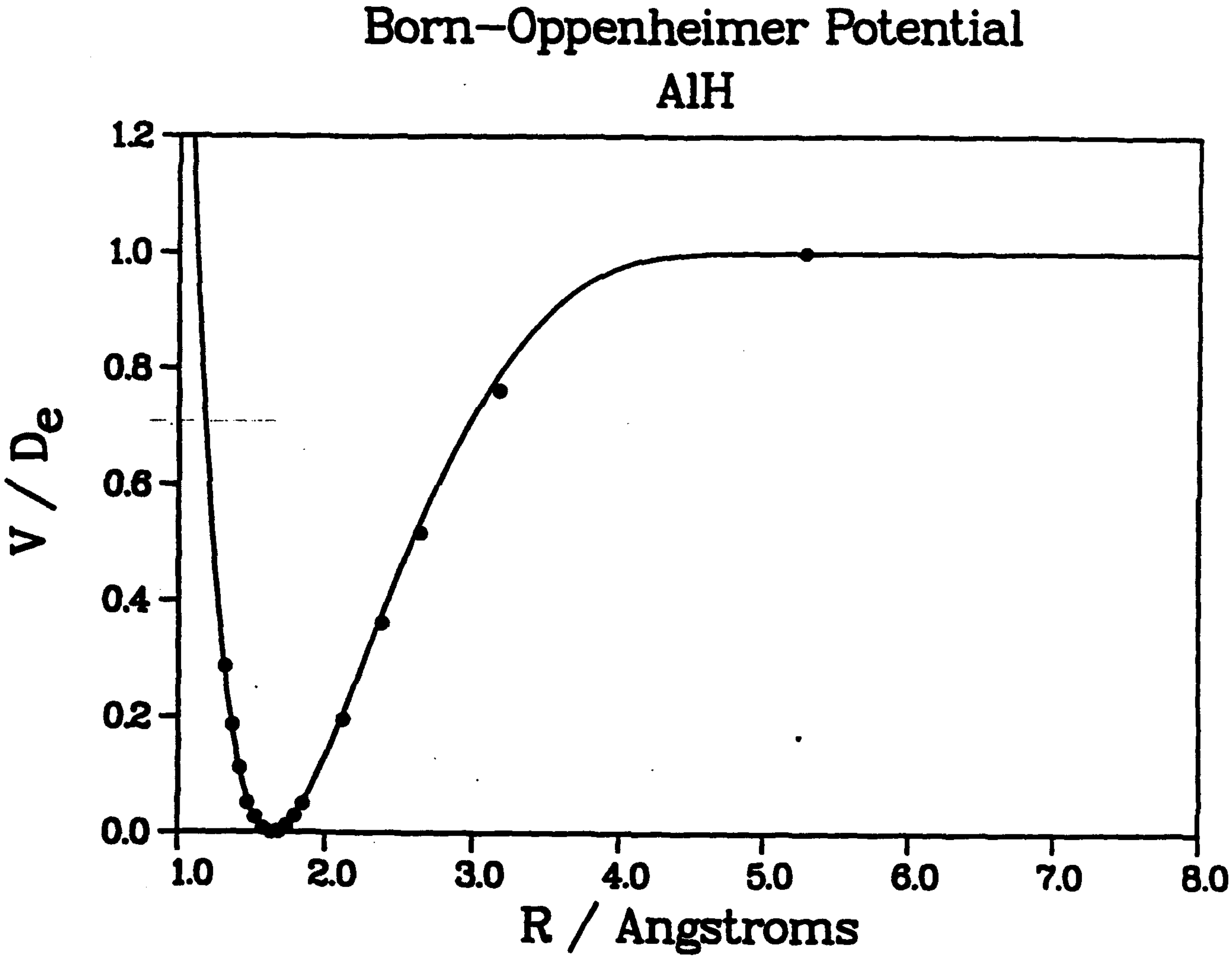


Figure 6: The AlH potential energy curve. The points are from a recent ab initio calculation.



generated B, C and Al atoms with each other as well as with small molecules such as H_2.

The first step in the development of an advanced propellant system is the identification of suitable new atomic and molecular fuels and oxidizers. Ultimately these light, energetic molecules will have to be synthesized efficiently and stored in condensed phases to make a viable propellant. Our work reported here concentrates on the initial steps in the process of advanced propellant design.

P. Publications (supported by grant F29601-91-C-0100).

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