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CORRELATION OF THE VIBRATIONS OF MOLECULES AND STABILITY IN ENERGETIC MATERIALS

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CORRELATION OF THE VIBRATIONS OF MOLECULES AND STABILITY IN ENERGETIC MATERIALS

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I. INTRODUCTION

Materials such as propellants and explosives, must by their nature contain tightly bonded groups of atoms which retain their molecular character until a sufficient stimulus is applied to cause dissociation. For the material to be "energetic", the dissociation is accompanied by an energy release which in turn triggers further dissociation leading to initiation or ignition. The desired macroscopic behavior is ultimately controlled by the interatomic forces. Only when it is possible to quantitatively describe the forces will it be possible to predict whether a given molecular structure will support an explosive reaction. The present inability to make such predictions represents one of the fundamental limitations to the advance of energetic materials science and technology.

At the 1970 and 1972 Army Science Conferences the authors of the present paper demonstrated that some of the dynamic, molecular properties of materials of the complexity of explosives and propellants could be elucidated if a comprehensive experimental and theoretical approach were employed (1,2). The present paper represents implementation and further refinement of the capabilities required to characterize the fundamental processes of interest in energetic materials. In particular, attention is focused on the correlation of interatomic forces and physical and chemical instability as manifested by changes in the dynamics of molecular groups in ammonium nitrate, ammonium perchlorate and the metal-azide salts.

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Ammonium nitrate (NH_4NO_3) is of considerable military interest because of its explosive properties. Furthermore it is cheap and available in enormous quantities so that its more wide-spread military use could, potentially, result in cost savings of many millions of dollars. The limited success of conventional approaches in providing a solution to problems associated with its use has lead to their examination with the techniques of the present program.

Ammonium perchlorate (NH_4ClO_4) is a compound used extensively in propellant formulations and may well be the most thoroughly studied of all energetic materials. This because of its military usefulness, but also because aspects of its behavior have general scientific importance. Despite the extensive study no coherent picture of the interrelationship between its molecular properties and macroscopic behavior had yet emerged. The results of the present investigation go far to rectify this failure.

The metal-azide salts form a family of compounds exhibiting chemical properties ranging from stable to highly unstable. For this reason comparison of the properties of different metal-azide salts and related compounds should provide some insight into the critical parameters involved in dissociation and its propagation.

Results for the compounds studied are presented in Section III. These are preceded in Section II by a discussion of experimental techniques including that of quasi-elastic neutron scattering which has not previously been employed for energetic materials. A brief introduction to the theory of lattice or molecular dynamics is also presented in Section II.

II. THEORY AND EXPERIMENTAL

Lattice dynamics is the term generally applied to the quantitative description of atomic and molecular motions in crystals and the forces of interaction which produce the motions. The usual method of expressing the equations of motions of the particles in a crystal is in terms of cartesian displacement coordinates X^n. With this coordinate system, the potential energy of the crystal in the adiabatic and harmonic approximation is written as (3):

$$2V = \sum_{\substack{\vec{n}-\vec{n}' \\ \alpha,\alpha'}} \Phi^{\vec{n}-\vec{n}'}_{\alpha,\alpha'} X^{\vec{n}}_{\alpha} X^{\vec{n}'}_{\alpha'}$$

where α numbers the S particles in the $\vec{n}$th primitive cell. The properties of the force constant matrix Φ are dependent upon the type of force field used to describe the interaction of the various particles and must be consistent with the symmetry of the crystal. The equations of motion to be solved are

$$\sum_{\alpha,\vec{\eta}} (M_\alpha M_{\alpha'})^{-1/2} \phi^{\vec{\eta}}_{\alpha\alpha'} e^{2\pi i\vec{q}\cdot\vec{\eta}} L_{\alpha' j}(\vec{q}) = L_{\alpha j}(\vec{q})\omega_j^2(\vec{q})$$

where $\omega_j(\vec{q})$ and $\hbar\vec{q}$ are, respectively, the vibrational frequency and quasi momentum of the jth mode phonon, $\vec{\eta} = \vec{n} - \vec{n}'$, and M_α is the mass of the αth atom. A "phonon" is the quantized plane wave of wavelength $\lambda = 2\pi/q$ and energy $E = \hbar\omega_j$, in terms of which the vibration is described. The quantity $\vec{L}_{\alpha j}(\vec{q})$, called the polarization vector, describes the magnitude and phase of the motion of the αth particle when the phonon (j,q) is excited. The determination of $\omega_j(\vec{q})$ and $\vec{L}_{\alpha j}(\vec{q})$ characterizes a vibration, and the functional dependence of these quantities is determined by crystal symmetry and the force field between particles. The measurement of these two functions is the aim of experimental lattice dynamics.

The point to be emphasized with regard to the conventional formulation of the description of lattice dynamics, outlined above, is that the atoms in real crystals <u>do not</u> experience a harmonic potential. The degree of anharmonicity is different for each type of atom and for each direction in which the atom moves. The importance of anharmonicity in the potential can be better understood when it is realized, for example, that in a purely harmonic crystal there is no thermal expansion, phonons do not interact, and phase transitions cannot occur. Of course, all of these occur in real crystals.

The degree of anharmonicity in the interatomic potential is best determined by the study of the changes in vibrational mode frequencies as a function of temperature and pressure. Anharmonicity affects the frequencies in two different ways. One of these is a purely volume dependent shift. The other shift - called the "self-energy" - arises from the direct interaction of the vibrational modes, and is both volume and temperature dependent. Experimentally, these anharmonic contributions can be separated only through a combination of spectroscopic studies performed at various temperatures and pressures, coupled with pressure-volume and temperature-volume measurements.

The current theory (4) which describes anharmonic effects, although formally straightforward, has been limited in application to a very few simple solids; details will not be presented here. In cases of large anharmonicities, the theory has not been fully developed.

One aspect of the general case of large anharmonic effects which has recently gained increasing importance, particularly in the case of ferroelectric materials, is that of displacive phase transitions. It has been found that a ferroelectric to paraelectric phase transition is often precipitated by a particular translational mode going "soft" (i.e. $\omega_j(\vec{q}) \rightarrow \sim o$ as $T \rightarrow T_c$) as a consequence of increasingly large amplitude vibration resulting from anharmonicity.

Rotatory motions of molecular groups (i.e. motions of atoms in a molecule about the center of mass of the molecule itself) are also expected to manifest the effects of anharmonic interactions. A direct consequence of the anharmonic potential in real crystals is the fact that for a molecular group, a rotatory motion of sufficiently large amplitude can result in a "permanent" reorientation of atoms in the molecule to equilibrium sites vacated by atoms of the same molecule. This is illustrated in Fig. 1 for an NH_4^+ ion. Only recently has this type of anharmonic effect come under quantitative examination.

Interatomic forces cannot be measured directly but are inferred from measurement of the $\omega_j(\vec{q})$ and $\vec{L}_{\alpha j}(\vec{q})$. (1,2) The principal experimental techniques used for lattice-dynamical studies are Raman and infra-red spectroscopy, and coherent neutron inelastic scattering (CNIS). Raman and infra-red spectroscopy provide information only for $\omega_j(q=o)$, whereas CNIS is not restricted in q. However, not all vibrational modes are observed by each experimental technique, but are subject to "selection rules". (2) In addition, neutron or x-ray diffraction, by which the crystal structure is obtained, are necessary pre-requisites to lattice-dynamical studies. In solids of the complexity of energetic materials, all experimental probes provide important information for determination of the interatomic forces.

A relatively new experimental technique - that of quasi-elastic neutron scattering (QNS) - has been employed for energetic materials for the first time. This type of probe gives direct information for the rotatory reorientations of molecular groups not readily obtainable by other means. Consequently, QNS provides a means of characterizing the appropriate interatomic potentials for this special type of dynamical behavior, which can range from free rotation to small amplitude rotatory vibration with no reorientation.

The QNS technique is sensitive to this entire range of behavior; however, it is the intermediate region consisting of rotatory vibrations for a period of time, τ, long compared to a vibrational period, followed by a reorientation which is of greatest interest. τ is generally referred to as the residence time.

In general, the QNS cross-section, $\sigma(\vec{Q},\omega)$ for an atom, is given by (3)

$$\sigma(\vec{Q},\omega) \sim \int d\vec{r} \int_{-\infty}^{\infty} dt \, \exp[i(\vec{Q}\cdot\vec{r}-\omega t)] \sum_i P_i(t)\,\delta(\vec{r}-\vec{r}_i)$$

where $\vec{Q}$ and $\hbar\omega$ are, respectively, the momentum and energy transferred by the neutron in the scattering process, $\vec{r}_i$ denotes the position of the scattering atom, and $P_i(t)$ is the probability of finding the atom at site i at time t given that it was at $\vec{r}_o=o$ at $t=o$. In the temporal region of interest, one can assume that the rotational jumps are instantaneous so that the particle is always at one of the equilibrium sites.

The $P_i(t)$ are then obtained in a relatively straightforward manner. Sköld has done this for a tetrahedral molecule with all four sites equivalent, i.e. equal τ's. (5)

We have extended the theory to the case more appropriate to NH_4ClO_4: $\tau_o \neq \tau_1 = \tau_2 = \tau_3$. This residence time distribution yields a QNS cross-section (6)

$$\sigma(Q,\omega) \sim \pi[1+3j_o]\,\delta(\omega) + [1-j_o][L(\alpha_1) + L(\alpha_2) + L(\alpha_3)]$$

where $j_o = \sin QR/QR$, $\delta(\omega)$ is the Dirac delta function,

$$L(\alpha_j) = \alpha_j/(\alpha_j^2 + \omega^2)$$

$$\alpha_1 = \frac{5}{3\tau_o} - \frac{1}{3\tau_1}$$

$$\alpha_2 = \frac{2}{3}\left(\frac{1}{\tau_o} + \frac{1}{\tau_1}\right)$$

$$\alpha_3 = \frac{5}{3\tau_1} - \frac{1}{3\tau_o}$$

and R is the jump distance; in ammonium, R = 1.78 Å.

In practice, the measured $\sigma(Q,\omega)$ consists of a resolution broadened $\delta(\omega)$ contribution superimposed on the Lorentzian components. The full-width-at-half-maximum (FWHM) of the composite distribution vs. Q gives a crude estimate of the character of the reorientation and the τs; a detailed analysis of the line-shapes at each Q is a more sensitive test of the model. Both approaches are used in the next Section.

III. RESULTS

A. NH_4NO_3

Ammonium nitrate crystallizes in as many as five different polymorphic forms at atmospheric pressure, and it is their existence that leads to serious technological problems for the utilization of NH_4NO_3 in military hardware. For example, the phase transition between phase IV (-18°C ↔ 32.3°C) and phase III (32.3°C ↔ 84.2°C) occurs at 90°F which is a temperature through which munitions in storage, during loading, or in the field are cycled by climatic and manufacturing conditions. One practical problem which arises is that the temperature coefficient for expansion of phase III is much larger than that of phase IV so extrusion of NH_4NO_3 through casings occurs, which, in turn, alters performance. The interest here is to determine the fundamental properties of NH_4NO_3 in its various phases, which will suggest methods by which, for example, the above problem can be eliminated.

At the 1972 Army Science Conference, the first complete structural study of NH_4NO_3 (IV) was reported. (2) Comparison of the detailed structure of phase IV and the partial determinations of the phase II and IV structures revealed that the occurrence of phase III was, in fact, anomalous. That is, a structural transition IV ↔ II involved much less rearrangement and less energetic processes than IV ↔ III or II ↔ III. From the microscopic point of view, a catalyst - known to be surface or occluded water (2,7) - was required for phase III to occur. To attempt to shed further light on this problem QNS was employed, for the first time, to examine the rotational dynamics of NH_4^+ in ammonium nitrate. (6)

Phases IV, III, II (84.2 ↔ 125°C) and I (125° ↔ MP) were studied after mild drying at 100°C ("wet") and after drying at 135°C ("dry"). Approximately 1% additional H_2O, by weight, was removed after redrying at the higher temperature. Powder neutron diffraction measurements were performed as a function of temperature to confirm earlier phase transition findings. QNS studies were made at temperatures of 24°, 45°, 75°, 95°, 120° and 130°C, wet and dry. Line shape analyses of the individual spectra have not been completed; however, FWHM vs Q plots are shown in Fig. 2 for phases IV and II, wet and dry. (6) The following conclusions can be drawn:

1. The powder diffraction measurements confirm the occurrence of phases IV, III, II and I in wet samples. Furthermore, drying at 135°C removes sufficient water to eliminate phase III so that the IV ↔ II transition occurs directly, at ~50°C.

2. The presence of a small amount of H_2O clearly affects the NH_4^+ dynamics in phase II. The nature of the change in the FWHM vs Q curves for phase II indicates shorter residence times and weaker (NH_4)-(NO_3) bonds in the wet sample than in the dry. It is believed that phase IV wet and dry would exhibit similar differences except that they are masked in our measurements by statistical uncertainties and insufficiently fine resolution.

3. Surface (or occluded) water in NH_4NO_3 causes a cooperative weakening of N-H···O hydrogen bonds throughout the bulk of the material. This weakening of H-bonds causes phase IV to become unstable at a temperature where phase II is not yet energetically favorable. This results in the formation of the anomalous phase III.

B. NH_4ClO_4

Ammonium perchlorate is, as indicated above, a most thoroughly studied material; nevertheless, the macroscopic properties are still far from understood. In particular, the peculiar decomposition behavior (8) in the neighborhood of the orthorhombic to cubic phase transition (513°K) is puzzling but clearly indicates that the crystal structure and the stability of intramolecular bonds are closely inter-related. It is toward elucidating the microscopic properties which cause this behavior that our studies of NH_4ClO_4 are ultimately directed. At the same time, the low temperature properties of NH_4ClO_4, although the subject of extensive scientific study for several years, have also remained uncertain. (9)

To clarify this long-standing problem, and to establish a framework within which to examine the high-temperature behavior, the microscopic properties have been examined in considerable detail in the 10°-300°K temperature range by means of neutron diffraction, QNS and Raman scattering.

Previous experimental work (i.e. NMR, Cv, IR, Raman and neutron transmission) has been analyzed to characterize NH_4^+ motions. (9) Based on assumptions that the reorientations occur entirely with one hydrogen fixed or with all four hydrogens bound equally (i.e. equal τ's), these studies have yielded potential barriers ranging from 0.2 to 2.0 kcal/mole. There has also been the suggestion of a possible phase transition in the 10°-100°K temperature range. The neutron diffraction data of the present work shows that NH_4ClO_4 retains its orthorhombic (Pnma space group) structure from 298° to 10°K. More interestingly, the principal axes of rotation and the rotational amplitudes of the NH_4^+ ions have been extracted and are summarized in Table I.

Table I.

Rotational Amplitudes of NH_4^+ in NH_4ClO_4

Temperature (°K)	Principal Axis	Amplitude (°)	Direction Cosines α	β	γ
	1	25.7	.6981	.0000	.7160
10	2	9.3	.0000	1.0000	.0000
	3	8.6	-.7160	.0000	.6981
	1	30.6	.6591	.0000	.7520
78	2	15.8	.0000	1.0000	.0000
	3	15.8	-.7520	.0000	.6591

The direction cosines, α,β,γ are the cosines of the angles between the principal axes of rotation and the x, y and z crystallographic axes, respectively. Fig. 1 shows the NH_4^+ ion and surroundings at 10°K as viewed along principal axes 1, the axis about which the largest rotational amplitude occurs. The 78°K result is quite similar, with somewhat larger amplitudes. The ellipsoids of thermal vibration (Fig. 1) indicate that H_3 and $H_{3'}$ see identical potentials while H_1 is more weakly bound and H_2 is more tightly bound.

Using the model described in Section II, QNS studies of NH_4ClO_3 at 78°, 105° and 130°K have been analyzed in great detail (6). Below 78°K, the broadening of the QNS peak quickly approaches that of the instrumental resolution function. As a first approximation, the QNS spectrum at each of five Q values for each temperature was least-squares fit with the resolution broadened theoretical scattering cross-section, adjusting τ_1 and τ_2 ($\approx \tau_3 = \tau_{3'}$). Under the assumption that the residence times, τ_i, are related to the rotational barrier height as $\tau_i = \tau_i \exp(+\epsilon_i/kT)$, activation energies $\epsilon_1 = 0.2 \pm 0.1$ kcal/mole and $\bar{\epsilon}_{2,3} = 0.85 \pm 0.1$ kcal/mole are obtained. The bar denotes an average barrier.

Raman scattering results (10) obtained at 18°K, 49°K and 82°K and higher temperatures for single crystal NH_4ClO_4 reveal changes both in the NH_4^+ intramolecular vibrational modes as well as the intermolecular (lattice) modes generally consistent with the QNS and neutron diffraction results. Of particular interest is the fact that three "soft" modes are observed in this material.

Fig. 3 shows the spectra of the B_{1g} and B_{3g} symmetry modes which become highly overdamped as temperature is increased from 18°K to 82°K. These modes are identified as NH_4^+ translational modes strongly coupled to rotations. As temperature increases, the rotational reorientations decrease the lifetime of the translational phonons leading to the overdamped behavior. Even more interesting is the "soft" mode behavior of the A_g perchlorate mode which occurs at 45 cm^{-1} at 298°K. The temperature dependence of this and another A_g mode is shown in Fig. 4. Based on preliminary neutron scattering results using the CNIS selection rules (2) the soft mode is identified as a perchlorate translational mode. The point to be noted in this case is that the softening of this mode begins to occur at the temperature ($\sim$100°K) where the NH_4^+ reorientation has become very frequent. This mode continues to soften as the phase transition temperature is approached. It has been speculated that the phase transition occurs when the perchlorates begin to "rotate freely"; the present result is consistent with this hypothesis. Furthermore, strong rotation-translation coupling is indicated for the perchlorate ions.

Several important conclusions can be drawn from our studies concerning the molecular properties of NH_4ClO_4:

1. There is no structural phase change from 10°K to 298°K.

2. The observed dynamics of the four NH_4^+ hydrogens are consistent neither with all hindering potentials identical nor with one hydrogen "infinitely" tightly bound as has been assumed elsewhere. Qualitatively, we find $\epsilon(H_1) \leq \epsilon(H_3) = \epsilon(H_{3'}) \leq \epsilon(H_2)$; quantitatively, $\epsilon(H_1) = 0.2 \pm 01$, $\epsilon(H_{2,3}) = 0.85 \pm 0.1$ kcal/mole.

3. The coupling between rotational reorientation and translational modes is manifested by the overdamped behavior of the NH_4^+ translational "soft" modes; also by the frequency shift of the perchlorate "soft" mode. These results, along with results for azides discussed in the next subsection, represent the first observation of "soft" modes in energetic materials.

C. Metal-azide Salts

The metal-azide salts were the first materials studied in a systematic way within the present program. (1) In terms of understanding the importance of anharmonic effects in energetic materials, the metal-azide salts provide numerous similar compounds with widely differing thermal and configurational stabilities.

The main aspect of our studies of metal-azide salts that we wish to present here concerns the elucidation of anharmonic interactions through the study of molecular dynamics under the combined effects of temperature and pressure. It should be mentioned that the first studies of this type were performed only a few years ago, and the number of compounds whose vibrational properties have been measured under pressure remains very limited. The pressure parameter is particularly important for the understanding of detonation phenomena because extremely high pressure precedes the propagating reaction wave. Also, as described in Section II, spectroscopic studies performed as a function of temperature and pressure provide the only means by which the purely volume dependent anharmonic forces and the "self energy" can be determined. Such studies have now been performed for the first time for a metal-azide salt, KN_3.

Fig. 5A shows the pressure dependence of the Raman-active lattice modes of KN_3. (12) It is clear that the rotatory E_g and B_{1g} mode (experimentally unresolved) is much more sensitive to the volume change than is the translational E_g mode. Volume and single-crystal temperature data for the rotatory E_g are combined in Fig. 6. (12) In this figure, V_o and ω_o correspond, respectively, to volume and vibrational frequency at 1 atmosphere pressure and 298°K; the "pressure domain" corresponds to increasing compression at constant temperature, the "temperature domain" corresponds to increasing temperature at constant pressure. If the self-energy part of the anharmonic interactions were small, the data points would fall along a single line in the temperature and pressure "domains." However, the data points in the temperature domain fall increasingly far from this line indicating that the mode-mode interactions involving the rotatory modes are quite significant. $\Delta\omega$ is the quantitative measure of these interactions.

TlN_3 is a crystal having the KN_3 structure at 298°K. However, with regard to chemical stability, TlN_3 appears to be transitional between stable salts such as KN_3 and unstable salts such as AgN_3. Structurally, TlN_3 is now known to occur in four different solid phases, all reversibly induced by variations in temperature and/or pressure. The existence of the high-pressure phase (III) was revealed through the present studies. (13) It should be mentioned that although, in general, the correlation of physical and chemical instability has not been established, the results described earlier for NH_4ClO_4 suggest that at least in some cases, a strong correlation does exist.

In Fig. 5B the pressure dependence of Raman-active modes in TlN_3 up to the II→III phase transition (8 kbar) is shown. These data can be compared with the results for KN_3 shown in Fig. 5A. In the TlN_3 case, a strong pressure dependence for both the rotatory and translational E_g symmetry modes occurs. This is attributed to a strong coupling between these modes which reduces the $R(E_g)$ mode frequency and also induces a pressure dependence in the $T(E_g)$ mode, compared to KN_3. Since no analagous phase transition occurs in KN_3, one must conclude that the $T(E_g)$-$R(E_g)$ anharmonic coupling in TlN_3 is a critical phase stability parameter.

With regard to chemical stability, an indication of the differences in interatomic forces for different azides is illustrated in Fig. 7. The azide-ion bending mode frequencies (ν_2) are plotted vs the heat of formation (ΔH_f°) for several metal-azide salts. (14) The thermal stability of these salts decreases, approximately, with increasing heat of formation. The ν_2 bending mode frequency clearly softens with decreasing thermal stability suggesting a correlation between chemical stability and mode-mode interactions.

IV. CONCLUSIONS

The present study represents an important advance toward achieving the goals of the present program. In earlier work, structural and molecular dynamical properties were characterized only at atmospheric pressure and ambient temperature. Some speculation was made concerning changes that might be expected as conditions were varied but no concrete results were obtained for verification. In the present work, vibrational properties of selected materials have been measured over a broad range of temperature and pressure. Rather significant results are obtained including the actual observation, for the first time, of "soft" modes in energetic materials. These modes represent a direct manifestation of anharmonic mode-mode coupling, and it is this type of coupling which provides the mechanism for intermolecular- to intramolecular-mode energy exchange which enhances the probability of bond dissociation. It is thus of very significant interest for energetic materials.

Furthermore, the present work suggests that rotational degrees of freedom may play a more important role in the physical and chemical stability of solids than has been believed. This is brought out in the case of NH_4NO_3 where the reorientational freedom of the ammonium ions is directly related to the existence of phase III. In NH_4ClO_4, the observed perchlorate soft mode shows a softening correlated with increasing NH_4^+ rotational freedom, and the behavior of the mode appears related to the occurrence of the phase transition. Such a correlation is definitely established in the case of TlN_3 where strong rotational-translational mode coupling is observed with definite mode softening as the phase transition is approached. With regard to chemical instability, the marked dependence of the rate of decomposition on the crystal structure of NH_4ClO_4 must be related to changing molecular dynamics. Among the azides, the correlation of the azide-ion bending mode and thermal instability is established.

In each of these complex materials it appears likely that the macroscopic properties of interest i.e. chemical and structural stability, are controlled primarily by a few, critical microscopic parameters. Although not yet explored systematically, we expect that by properly choosing an additive or impurity atom, control of the critical parameters could be achieved. This is an area now ripe for experimental investigation. Furthermore, recent results obtained by computer molecular dynamics studies (15) indicate that the coupling of this technique with state-of-the-art experimental work should, in time, provide a complete understanding of the properties of interest.

In summary, the present work shows that the capability of examining certain microscopic properties of energetic materials has been advanced considerably. More importantly, correlations between molecular dynamics, anharmonicity, and militarily important macroscopic properties are clearly established. Finally, the comprehensive approach employed in these studies has yielded results of significance not only for energetic materials but for all complex materials.

V. ACKNOWLEDGEMENTS

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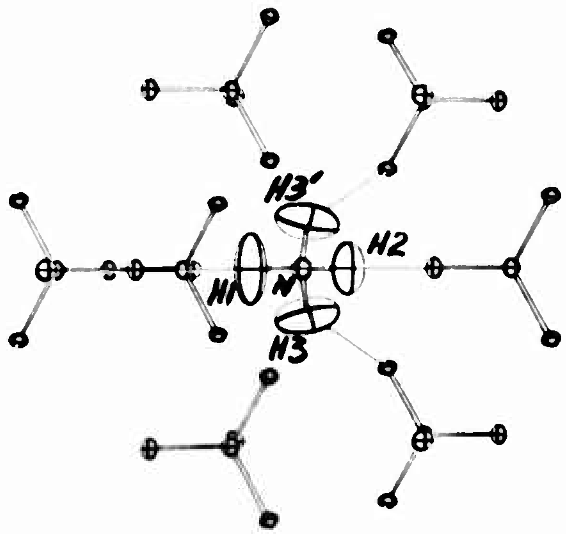


FIGURE 1: NH_4^+ ion and surroundings in NH_4ClO_4 at 10°K as viewed along principal axis 1 (see text). A rotary displacement can occur, for example, about the H1-N bond such that H2→H3 site, H3→H3' site and H3'→H2 site without changing the overall molecular configuration. The ellipsoids represent the r.m.s. amplitudes of vibration.

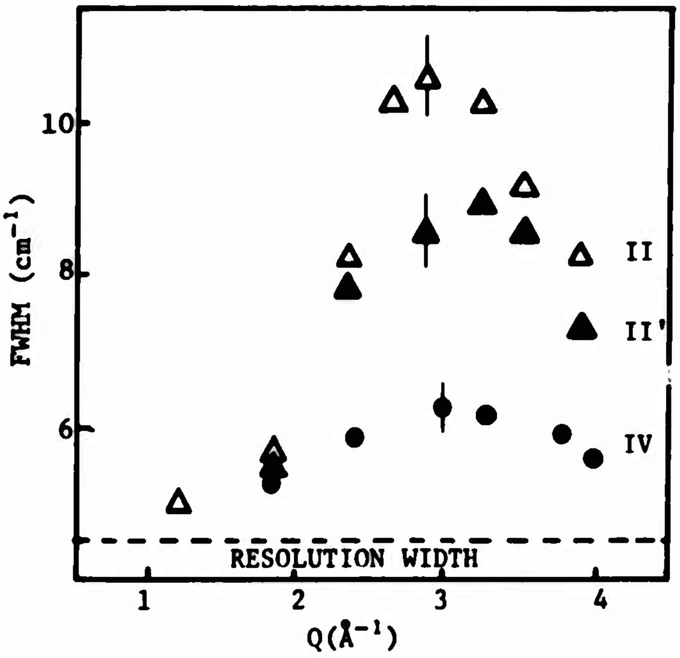


FIGURE 2: Full width at half maximum vs momentum transfer for NH_4NO_3 in phases II and IV. The prime denotes the dried sample.

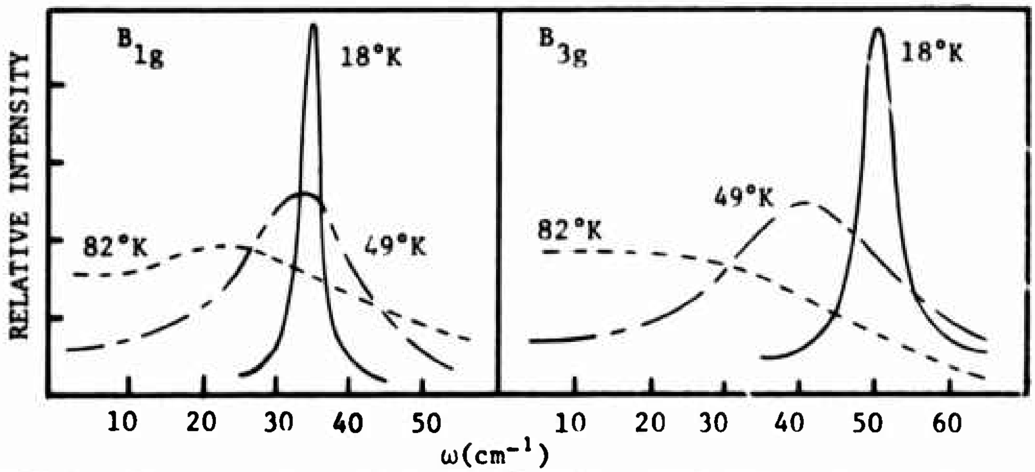


FIGURE 3: Raman spectra of the NH_4^+ soft modes observed in ammonium perchlorate.

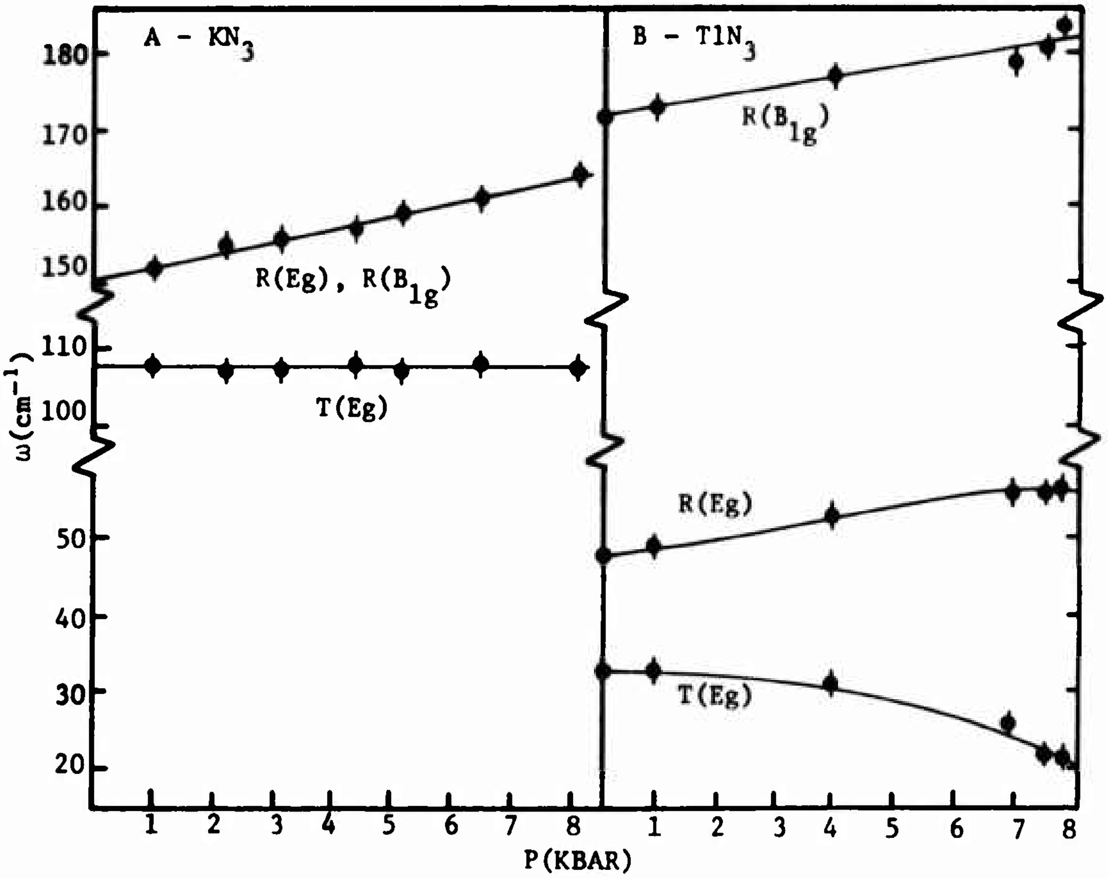


FIGURE 5: Pressure dependence of lattice modes.

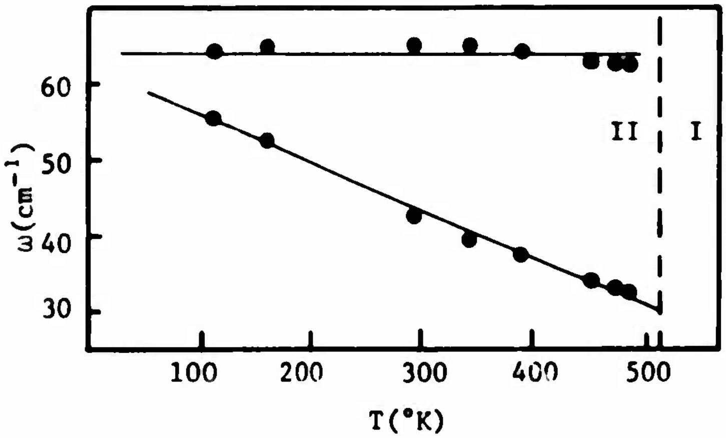
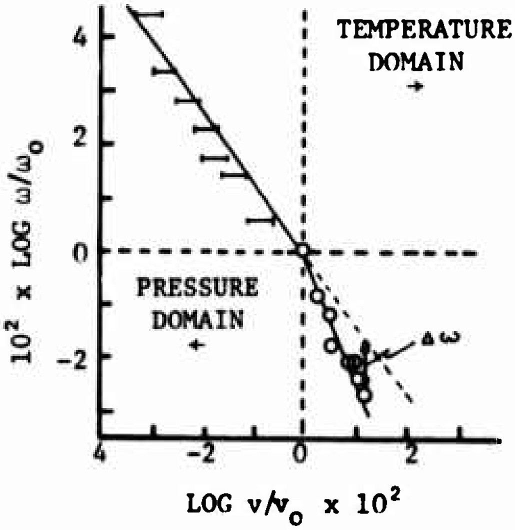


FIGURE 4: Temperature dependence of the Ag symmetry-species ClO_4^- vibrational modes. The orthorhombic to cubic phase transition is at 513°K. ω, here, represents the peak position.

FIGURE 6: Log ω/ω_o versus log v/v_o for the rotary Eg mode in KN_3. (See text for details.)



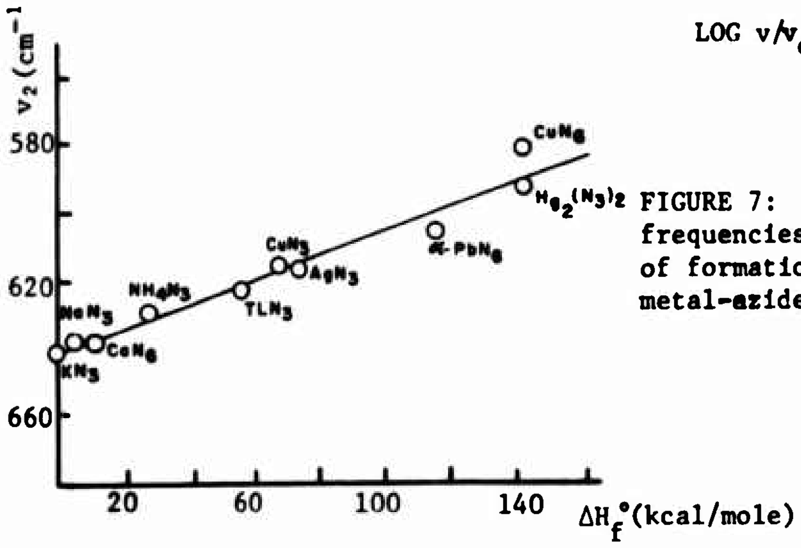


FIGURE 7: Bending mode (ν_2) frequencies versus the heat of formation for a number of metal-azide salts.