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TITLE: VIBRATIONAL FREQUENCY SHIFTS OF FLUID NITROGEN FUNDAMENTAL AND HOT BAND TRANSITIONS AS A FUNCTION OF PRESSURE AND TEMPERATURE

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VIBRATIONAL FREQUENCY SHIFTS OF FLUID NITROGEN FUNDAMENTAL AND HOT BAND TRANSITIONS AS A FUNCTION OF PRESSURE AND TEMPERATURE*

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ABSTRACT

Coherent anti-Stokes Raman scattering (CARS) and spontaneous Raman spectroscopy have been used to obtain vibrational spectra of shock-compressed and static high-pressure fluid nitrogen, respectively. Vibrational frequencies were obtained from the CARS data using a semiclassical model for these spectra. Spontaneous Raman vibrational frequencies were determined by fitting data using a Lorentz shape line. A functional form was found for the dependence of the vibrational frequency on pressure and temperature to 40 GPa and 5000 K, respectively. The result is compared to a recent theoretical model.

KEY WORDS

CARS, diamond cell, nitrogen, pressure standard, Raman spectra, shock compression

INTRODUCTION

The development of pressure scales for use at high temperatures is currently the source of considerable interest and vexation. Fluid nitrogen has a number of properties that make it an attractive high-temperature spectroscopic pressure standard. In this paper we reanalyze lower pressure and temperature static data (Zinn et al., 1986) and combine it with dynamic (shock wave) data (Moore et al., 1989) to derive a nitrogen vibron pressure scale valid from the melting curve to 40 GPa and 5000 K. The agreement of these data sets with each other and the small scatter within each data set strongly support establishing a standard.

DETERMINING HIGH-PRESSURE/HIGH-TEMPERATURE STANDARD

The dependence of the Raman shift frequency, ω , on pressure, P , and temperature, T , was obtained by empirically expanding, ω_e , and the first anharmonic term, $\omega_e x_e$, (Herzberg, 1950) as follows:

$$\omega = \omega_e + a_1 P + a_2 P^2 + a_3 T + a_4 T^2 - 2(\gamma_e + 1)(\omega_e x_e + a_5 T) \quad (1)$$

Here γ_e is the lower state vibrational quantum number and $\omega_e x_e$ is taken as suggested from experimental results to be the gas-phase value of 14.456 cm^{-1} . ω_e was adjusted to 2357.3 cm^{-1} to agree with the observed Raman shift frequency of 2328.1 cm^{-1} at 0.00025 GPa and 82.9 K. The coefficients a_1 - a_5 , listed in Table I, were determined from a least-squares fit of Eq. 1 to 87 static and dynamic data points (Zinn et al., 1986 and Moore et al., 1989). The numbers in parenthesis given

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for each coefficient are the standard errors for that coefficient obtained from a multi-variable regression analysis (Snedecor and Cochran, 1967). The standard error of the fit was 0.9 cm^{-1} , less than the experimental uncertainty. Figures 1 and 2 show the measured frequencies and, by a small line segment, the empirically-calculated frequency at the corresponding experimental pressure and temperature.

Table I. Coefficients and standard errors.

a_1	$2.9680 (0.0469) \text{ cm}^{-1}/\text{GPa}$
a_2	$-0.03476 (-0.00101) \text{ cm}^{-1}/\text{GPa}^2$
a_3	$-0.3276 \cdot 10^{-2} (0.0419 \cdot 10^{-2}) \text{ cm}^{-1}/\text{K}$
a_4	$-0.5634 \cdot 10^{-6} (0.0739 \cdot 10^{-6}) \text{ cm}^{-1}/\text{K}^2$
a_5	$-0.694 \cdot 10^{-4} (0.089 \cdot 10^{-4}) \text{ cm}^{-1}/\text{K}$

Fig. 1. Raman shift vs pressure for 0-1 transition. The open circles are data obtained using a diamond anvil cell and spontaneous Raman scattering; the solid circles were obtained using shock compression and CARS; the solid square at 0.00025 GPa was obtained using CARS. Solid lines are isotherms obtained from Eq. (1); the temperature is given alongside each isotherm. The dotted line is a 2000-K isotherm from Belak et al. (1988).

The pressure and temperature range over which the frequencies given by Eq. 1 can be expected to be valid are depicted graphically by isotherms for the fundamental transition and for the 1-2 hot band. Because Eq. 1 is based solely on experimental data, its use outside the recommended range is discouraged. Also shown for comparison in Fig. 1 is the Raman frequency along a 2000 K isotherm from an empirical approximation to Monte Carlo calculations by Belak et al. (1988). As noted by the authors, the Monte Carlo calculations give frequencies that are slightly larger than experimental results, with the discrepancy becoming greater at increasing pressures. Possible reasons for this difference were briefly discussed in a previous publication (Moore et al., 1989).

SUMMARY

Using high-pressure diamond-anvil cell and shock-wave data an empirical expression was obtained for the liquid N_2 vibrational Raman frequency shift with pressure and temperature. A multi-variable regression analysis was used to determine the standard error of the coefficients. It is suggested that this expression can be used over the wide range of pressures, temperatures, and transitions as a standard, both for theoretical calculations and for determining thermodynamic parameters for a variety of experiments, e.g., laser heating in a diamond-anvil cell. We are presently using this calibration to improve the accuracy of the fluid- δ nitrogen phase boundary. In using this standard, it is suggested that readers contact the authors to determine if the standard has been improved by the addition of new data.

Fig. 2. Raman shift vs pressure for 1-2 transition. The solid circles were obtained using shock compression and CARS. Solid lines are isotherms obtained from Eq. (1); the temperature is given alongside each isotherm. Ambient pressure data point (solid triangle) is from Herzberg (1950).

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